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## CONTENTS.

PAGE.

Proceedings ..... (19)–(20)

PAPERS.

The Quantitative Determination of Carbohydrates in Food-Stuffs. By W. E. Stone ..... 183

A New Calibrated Weighing Flask. By George L. Heath ..... 198

The Velocity of the Reaction between Ferrous Chloride, Potassium Chlorate, and Hydrochloric Acid. By A. A. Noyes and R. S. Wason ..... 199

The Oxides of Tungsten. By En. D. Desi ..... 213

The Distribution of the Precious Metals and Impurities in Copper and Suggestions for a Rational Mode of Sampling. By Edward Keller ..... 243

Recovery of Waste Platinum Chloride. Contributed by H. W. Wiley 258

Standard Iodine Solution for Sulphur Determinations. By Edward K. Landis ..... 261

Note: Notes on An Analytical Investigation of the Hydrolysis of Starch by Acids ..... 261

New Books: Commercial Organic Analysis; A Brief Introduction to Qualitative Analysis; Lecture Notes on Theoretical Chemistry; Précis d'Analyse Chimique; Studies in Chemical Dynamics; Principles and Practice of Agricultural Analysis; A Manual of Quantitative Chemical Analysis for the Use of Students; Engineering Chemistry ..... 263

Books Received ..... 274

REVIEW OF AMERICAN CHEMICAL RESEARCH ..... 29–48

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PAPERS ACCEPTED FOR PUBLICATION:

Periodides of Pyridine. By P. F. Trowbridge.

Sodium Perioxide as a Third Group Reagent. By S. W. Parr.

Improvement in Drying Chambers. By J. L. Beeson.

Improvements on Dr. Squibb's Volumetric Method for Estimating Acetone. By Lyman F. Kebler.

Modification of the Thallioquin Test for Quinine. By F. S. Hyde.

Variations in the Composition of Red Lead. By Durand Woodman.

Determination of Potash and Phosphoric Acid in Fodders. Contributed by H. W. Wiley.

Note on the Volatility of Boric Acid; Separation of Boric Acid from Phosphoric Acid; Estimation of Boric Acid in Foods. By L. de Koningh.

Sketch of Dr. Theodore George Wormley. By Edgar F. Smith.

The Insoluble Carbohydrates of Wheat. By H. C. Sherman.

Compounds of Metallic Hydroxides with Iodine. By Theodore Rettie.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

# THE QUANTITATIVE DETERMINATION OF CARBOHYDRATES IN FOOD STUFFS.

BY W. E. STONE.

Received February 2, 1897.

IN various articles published by the author[1] during the past ten years, attention has been called to the character of the composition of the so-called "nitrogen-free extract" of food materials. Other writers[2] have also discussed the same subject and numerous specific researches have contributed a constantly increasing amount of definite knowledge bearing upon the matter. As a result, it is now generally recognized that that portion of food material broadly included under the term "nitrogen-free extract," consists of a considerable number of definite chemical compounds, mostly of the nature of carbohydrates, but of such evident variation as regards their food value or digestibility, as well as their chemical and physical properties, that it is highly inconsistent, if not absurd, to continue to regard them as of homogenous character or worth in food valuation.

When one refers to the very great number of food analyses now on record and notes how large a proportion of all vegetable foods consists of nitrogen-free extract, he cannot escape the thought that a more definite knowledge of this group of bodies

[1] *Am. Chem. J.*, **13**, 73; **14**, 9; **15**, 653; **15**, 660; *J. Anal. Appl. Chem.*, **5**, 421; *Agri. Sci.*, **2**, 315; **7**, 6; U. S. Dept. Ag. Div. Chem., Bull., **28**, 125; *Ber. d. chem. Ges.*, **23**, 3791; **24**, 3019; **25**, 563; *Proc. Am. Asso. Advancement of Science*, **31**, 159; *Proc. Soc. Promotion of Agr. Science*, 1890.

[2] See articles by Tollens and his colleagues in *J. f. Landwirtschaft, Versuch-Stationen*, etc.; E. Schulze, *Ber. d. chem. Ges.*; and Cross and Bevan, *J. Chem. Soc.*

is necessary, if any value is to be attached to work of this kind. Occasionally a statement of analysis may be found which refers to carbohydrates instead of nitrogen-free extract, but the same thing is meant in either case, and the results have been obtained by the same methods. In comparatively few cases is there any record of any analyst having attempted to estimate directly in a food analysis any of the various substances included under nitrogen-free extract; and anything like a complete determination of all these has rarely if ever been attempted. The present method, as almost universally followed for estimating the constituents of foods, consists in directly determining the amounts of moisture, ash, fat, fiber, and proteids in the material and the difference between the combined percentages of these and 100 is called nitrogen-free extract. This amounts, in many of the most important food materials, to more than fifty per cent. of the whole. It includes, of course, all of the known carbohydrates and doubtless other materials of unknown character, but gives no clue to the relative proportion of any of them.

In brief, the present stage of food analysis leaves us largely ignorant as to the character and value of the principal constituents of many of the most important foods. Little wonder that many have come to regard the ordinary food analysis as contributing little information regarding the actual food value of any material. It certainly affords no means of ascertaining whether the sixty to eighty per cent. of nitrogen-free extract in grains is to be valued as an easily digested carbohydrate or a practically valueless gum or hemicellulose; it tells us nothing as to the presence or absence of sugar or soluble forms of starch or their relative proportions; it furnishes, in short, no accurate information as to the quantity or quality of the carbohydrates which constitute one of the three essential classes of nutrients and are among the chief constituents of vegetable foods.

Recent contributions to our knowledge of the carbohydrates have revealed to a surprising degree not only their specific chemical and physical properties, but indicate even more subtle and delicate distinctions as regards their physiological values; their susceptibility to organized and unorganized ferments; their origin and functions in the growing plant, etc. The time is therefore fully ripe when analytical methods ought to show equal progress

and differentiate sharply between the various kinds of carbohydrates. That something of the kind is highly important will be acknowledged, I think, by every chemist who has to deal with this subject. That such a practice is not already established is due, without doubt, to the lack of general information with regard to the properties of these different substances and the absence of an accurate and easily performed method of separately estimating their amounts.

Any method of analysis intended to apply to this case and which shall be expected to become generally adopted, must have the qualities of simplicity and accuracy. It must be borne in mind, however, that the class of materials included under the general head of nitrogen-free extract, are of such a nature as to render them in many cases difficult of accurate determination.

It is believed that the method here presented satisfies these requirements better than any yet proposed. Although as here presented, some details have been modified, the general method has been employed in an investigation upon the carbohydrates of wheat and maize, the results of which have been published by the U. S. Department of Agriculture as Bulletin 34 of the Office of Experiment Stations. The analytical data presented here are selected in part from this report by permission.

The carbohydrates to be found in food materials of a vegetable origin, include sugars of different kinds, starch in various modifications and a certain kind of material, intimately associated with the true cellulose, variously designated as gums, pentosans, hemicelluloses, oxycellulose, and finally the cellulose itself.

For the determination of many of these substances, methods already exist which permit of very fairly accurate determinations, but these methods, as a rule, assume that all other carbohydrates shall be absent so that their application to a material containing several of these substances would lead to serious errors and false conclusions. The most notable example of this is the determination of starch, the ordinary method for which consists in heating the starch containing materials with dilute acids and determining the sugar thus produced by titration with Fehling's solution.

This, as well as other methods for the determination of starch in the absence of other carbohydrates, is of practically sufficient

accuracy, but as has been shown, none of these mothods are applicable to the determination of starch in the presence of such other carbohydrates as the pentosans or the hemicelluloses.[1]

Again, the methods proposed for the determination of the pentosans are all based upon a destructive distillation of the original material with strong acids and the subsequent determination of the furfurol thus produced. However accurate this final determination may be according to one or the other of several methods, it is obvious that only an approximate knowledge is obtained as to the actual amount of pentosans present in the original material.

It seems also desirable that any plan for the differentiation of carbohydrates in any given material, should, so far as possible, approximate the selective action of the digestive organs in dealing with these same materials. This principle has been recognized in the familiar Weender method for the estimation of crude fiber, which has so long been made use of by food chemists. For example, those substances which are readily soluble in mild reagents will evidently be more easily digested and assimilated than those which are practically insoluble, so that although we may not possess complete knowledge of these same insoluble substances or of their value as food materials, we may still separate them in our analytical tables from those of which we do know more and which evidently have a greater food value.

The following method for the detailed determination of the carbohydrates in vegetable materials is based upon the successive treatment of the same sample: 1, with boiling alcohol to remove sugars; 2, with cold water to remove dextrin and soluble forms of starch; 3, with diastase or malt infusion to remove starch; 4, with dilute boiling hydrochloric acid to convert the gums, pentosans, hemicelluloses, etc., into soluble, reducing sugars; 5, with boiling 1.25 per cent. sodium hydroxide, as is customary in the determination of the crude fiber by the Weender method, leaving behind crude fiber.

In all of these successive operations, linen filters are to be used in order to facilitate the subsequent removal of the sample. With very fine starchy materials it may be advisable to fold a paper filter within the linen one.

[1] This Journal, 16, 726.

In each of the above successive extracts the respective carbohydrates may be estimated by optical or chemical methods, although they are all susceptible of titration by Fehling's solution in the ordinary way.

This method presents certain marked advantages:

1. It permits of the estimation of these constituents in one and the same sample.

2. The process consumes comparatively little time.

3. The final determinations are made by methods already in common use, well understood, and capable of being accurately performed by persons of no great analytical skill.

4. If, by any error of manipulation, any portion of the carbohydrates sought for at any stage escapes solution, it can scarcely fail to be obtained at the succeeding stage, and so there can be no failure to sum up in the end all of the carbohydrates actually present. For instance, any sugar escaping solution in alcohol would be removed by the subsequent treatment with water. Any starch not dissolved by the malt extract would certainly be removed in the subsequent treatment with dilute acid.

5. No violence is done to our present classification of food constituents, only those portions not heretofore classified being separately estimated and recorded. Even the crude fiber remaining after this treatment would be fairly comparable with that determined by the Weender method.

The successive operations may be outlined as follows:

1. The material being finely powdered or grated, from 50 to 100 grams, according to its nature, are accurately weighed and boiled with 500 cc. of strong alcohol, under a reflux condenser, during two hours, or the material may be extracted with boiling alcohol in a Soxhlet extractor. The sugars are thus dissolved and removed by filtering off the alcoholic extract. If this contain only sucrose it may be brought to a given volume and estimated in the polarimeter. If more than one kind of sugar, as for instance sucrose and invert sugar, are present, the alcohol may be carefully evaporated, the sugars taken up in water to a given volume and estimated by titration with Fehling's solution before and after inversion, according to the ordinary treatment in such cases.

2. *The residue from the alcoholic extraction* may contain carbo-

hydrates soluble in water, as for instance soluble starch and dextrin, which are specially to be considered in materials which have been subjected to the action of heat. To this residue, therefore, is added 500 cc. of water and the whole allowed to stand eighteen to twenty-four hours with frequent agitations. The watery solution is then filtered, using a linen filter. With ordinary materials where only dextrin-like substances are to be expected, this filtrate may be evaporated to a small volume, inverted with dilute acids, and titrated with Fehling's solution in the ordinary way. If, however, the solution contain soluble starch in any of its forms, which may be recognized by the iodine test, a further distinction between this starch and dextrin becomes necessary.[1] The watery solution is brought to a volume of 200 cc., and of this an aliquot part is inverted with dilute acid and titrated with Fehling's solution in order to determine the total carbohydrates in the solution. Another aliquot part may be treated with an excess of a solution of barium hydroxide, which precipitates the soluble starch. In the filtrate from this precipitate, the dextrin may be determined by inversion and titration as before. The difference between the dextrin and the total carbohydrates determined in the first aliquot portion may be considered as soluble starch. The use of barium hydroxide for the estimation of the soluble starch directly, according to Von Asboth's method, is not permissible in this place because there are other substances in solution besides starch, which seem to combine with the alkali.[2]

3. *The residue from the aqueous extract* of the material is now brought to an air-dried condition and its weight determined in order to establish its quantitative relations to the substance as originally weighed out. This step is advisable because smaller portions are more conveniently employed for the subsequent operations.

This material now contains the starch and other insoluble carbohydrates. Two grams are weighed, 100 cc. of water added

[1] By soluble starch is meant starch soluble in water but still giving the characteristic blue color with iodine, in distinction from some of the more completely broken down forms of starch, like dextrin, which no longer give blue or purple colors with iodine. In only rare cases would it be necessary to make this distinction.

[2] It is thought that barium hydroxide combines with the albuminous substance in solution. At least a much larger amount is precipitated than can be accounted for by the total amount of carbohydrates present.

and boiled thoroughly for thirty minutes in order to convert the starch into a soluble form, then cooled to 60° C. In the meantime an infusion of malt has been prepared as follows: Ten grams of finely ground fresh malt are covered with fifty cc. of water and kept at an ordinary temperature, with frequent agitation, from two to three hours, filtered, and ten cc. of the infusion added to the starch paste, cooled as above.

The starch is subjected to the action of malt extract at a temperature not exceeding 65° C. from two to three hours, or until the blue starch reaction with iodine disappears. The solution is filtered on a linen filter and washed thoroughly with hot water. In many cases this filtration will be facilitated by previously heating the solution to boiling and filtering hot. The residue on the filter should give no starch reaction with iodine. The filtrate is evaporated to 100 cc., transferred to a 200 cc. flask, receives ten cc. of concentrated hydrochloric acid, and the flasks with contents kept at the temperature of a boiling water bath for one hour in order to convert all of the malt sugar into dextrose. The solution is then neutralized, made up to a volume of 200 cc., and titrated with Fehling's solution. A correction must of course be employed for the amount of sugar introduced in the malt extract.

4. *The residue from the malt extraction* still contains the gums, pentosans, hemicelluloses, and true cellulose. It is carefully removed from the filter, receives 100 cc. of water and two cc. strong hydrochloric acid, and is heated to boiling under a reflux condenser or in a water bath for one hour.

The action of the acid converts the gum and pentosans into reducing sugars, which may be regarded as xylose.[1] This is then filtered, neutralized, made up to 200 cc. and titrated with Fehling's solution.

5. We have now reached a stage corresponding to that attained in the determination of crude fiber by the Weender

[1] Repeated examinations of the character of this material shows that in most of the fibrous or woody vegetable materials it is xylan and yields on hydrolysis mainly xylose. This is the case especially in all materials containing any considerable amount of hydrolyzable carbohydrates of this kind, although in some special cases mannose, galactose, or arabinose have been noted as products of this treatment. It is thought sufficient, however, for all general purposes to regard this product as xylose, since the error introduced by the varying reducing coefficients of small amounts of the other sugar would be nominal.

method after the material has been boiled with one and one-fourth per cent. sulphuric acid. It remains, therefore, to treat this residue with 1.25 per cent. sodium hydroxide, to filter, dry, weigh, ignite and weigh again, in order to obtain what is commonly known as "crude fiber."

It is necessary now to consider the accuracy of each of these steps in detail, and to present examples of their application. For the purpose of illustration the following materials have been examined according to the plan here presented: Wheat, two samples; wheat flour, two samples; maize; bread made from each of the samples of whole wheat, flour, and maize; sugar beets, and a sample of timothy hay.

### 1. THE ESTIMATION OF SUGARS BY EXTRACTION WITH BOILING ALCOHOL.

It is hardly necessary to discuss this method since it is the generally accepted way of separating sugars from other materials either for qualitative or quantitative analysis. All of the ordinary sugars are soluble in boiling alcohol of ninety-five per cent. strength, especially when sufficient volume is employed as is the case in the specifications of the method here presented. It is even applicable to fresh materials, such as the sugar beet, potato, etc., in the presence of a large amount of moisture.

In the treatment of many materials, the hot alcohol also dissolves waxes and oils, which are readily removed by evaporating the solution nearly to dryness and then taking up in water. The polarimeter may be employed in many cases for determining the sugar thus extracted, in preference to the method of inversion and titration.

The following examples will serve to show how sugars, in small or large quantities, may be determined in a variety of materials and with accuracy, by means of this method:

SUGAR OBTAINED BY EXTRACTION WITH BOILING ALCOHOL.

| | Sucrose. Per cent. | Invert sugar. Per cent. |
|---|---|---|
| Wheat I | 0.51 | 0.08 |
| Wheat II | 0.72 | 0.00 |
| Wheat flour I | 0.18 | 0.00 |
| Wheat flour II | 0.20 | 0.00 |
| Maize | 0.27 | 0.00 |
| Sugar beet (Fresh) | 8.38 | 0.07 |
| Hay (Timothy) | 2.53 | 0.00 |

| | Sucrose. Per cent. | Invert sugar. Per cent. |
|---|---|---|
| Bread (Whole wheat I) | 0.05 | 0.32 |
| Bread (Whole wheat II) | 0.06 | 0.37 |
| Bread (Wheat flour I) | 0.01 | 0.10 |
| Bread (Wheat flour II) | 0.15 | 0.38 |
| Corn cake (Maize) | 0.16 | 0.19 |

2. THE ESTIMATION OF DEXTRIN AND SOLUBLE STARCH.

These materials, while insoluble in alcohol, are readily dissolved in water at ordinary temperature.

Usually grains and seeds in their natural condition contain very small quantities of materials of a carbohydrate nature, insoluble in alcohol and soluble in cold water which it is sufficient to designate here as dextrin. Some attempts to identify these bodies in a more specific manner, have been made. In this place, however, it is only necessary to say that they are readily changed into sugars by inversion with acids and behave, to all intent and purpose, like dextrin. If, however, the material has been subjected to heat or friction, as in the grinding of corn or flour, or to the action of acids, then a portion of the starch may have been changed into soluble forms and will accompany the dextrin in the watery solution. The presence of such starch will be readily detected by means of the blue color produced with iodine.

In the absence of such starch, it is sufficient to estimate the dextrin by inversion with acids. When, however, soluble starch is present, the separate estimation of the two becomes a more difficult matter. Ordinarily the small amount of dextrin would render a separate estimation of the two hardly necessary, in which case the watery extract might be at once inverted with acids and the total soluble carbohydrates estimated in this way.

Evidently there will be little occasion to assign different values to these two forms of starch products even after they are separately estimated. If desirable, however, the starch may be completely precipitated with barium hydroxide, according to the plan proposed by Von Asboth, and a separate estimation made as indicated above.

These separations have been made in some of the analyses presented below, and there is no reason to doubt that they are sufficiently accurate.

DEXTRINS AND SOLUBLE STARCH EXTRACTED BY COLD WATER.

| | Dextrin. Per cent. | Soluble starch. Per cent. |
|---|---|---|
| Wheat I | 0.27 | 0.00 |
| Wheat II | 0.41 | 0.00 |
| Wheat flour I | 0.90 | 0.00 |
| Wheat flour II | 1.06 | 0.00 |
| Maize | 0.32 | 0.00 |
| Sugar beet (Fresh) | 0.35 | 0.00 |
| Hay | 1.18 | 0.00 |
| Bread (Whole wheat I) | 0.68 | 1.37 |
| Bread (Whole wheat II) | 0.23 | 2.36 |
| Bread (Flour I) | 0.27 | 1.99 |
| Bread (Flour II) | 0.91 | 1.74 |
| Corn cake (Maize) | 0.00 | 2.80 |

### 3. THE ESTIMATION OF STARCH BY TREATMENT WITH MALT EXTRACT.

The residue from the preceding treatment consisting of many grams of material, is too bulky for subsequent operations. In order, therefore, to secure smaller portions of definite quantitative relations to the original fifty or one hundred grams taken, these residues are desiccated, weighed, and the amount of dry matter contained therein is determined. The proportion between this dry matter and that in the original material may then be established. From this, then, two grams are taken for the determination of starch and other remaining carbohydrates.

Many methods have been proposed for the determination of starch, any of which are fairly satisfactory when applied to starch in the absence of the other carbohydrates. A review of these methods and comparison of their values will be found in a former paper by the author,[1] and also in papers by H. C. Sherman[2] and by P. Hibbard,[3] but all of these methods give inaccurate results when applied to materials which contain any of the pentosans or gums or easily hydrolyzable forms of cellulose, since these latter materials are affected in the same way as starch and give similar products with the same reagents.

They are not, however, appreciably affected by the action of diastase,[4] and thus far it appears that this is the only agent which

[1] This Journal, 16, 726.

[2] *School of Mines Quarterly*, Columbia College, 17, 356.

[3] This Journal, 17, 64.

[4] The somewhat obscure action of malt extract on cellulose mentioned by Brown and Morris, as well as a similar action upon hemicelluloses, is of very uncertain extent under any conditions and is practically checked at 60°. J. Grüss: *Wochenschr. Brauerei*, 1895, 1257.

may be employed for the accurate separation of starch from these other substances.

As to the efficiency of this method for the complete removal of starch, there seems to have been some question. It also appears from recent investigation by the author that not all starches are affected in the same manner or degree by diastase. It may be found necessary in different cases, to subject the material to the action of diastase for a longer or shorter time. The operation, however, is wholly within the control of the analyst, since the final extraction of starch from the material can be detected by the iodine reaction. Being once in solution, it is then readily separated from the insoluble residue and converted into sugar by the action of dilute acids as above described.

The following table shows the results obtained upon the material previously extracted and examined for other carbohydrates as described above.

These data were obtained by the use of more dilute acids for the hydrolysis of the malt extract, than is recommended above. The percentages are therefore somewhat lower than those usually ascribed to these materials. With the strength of acid prescribed there is no difficulty in obtaining complete conversion of the starch products into sugar.

NORMAL STARCH DISSOLVED BY MALT EXTRACT.

| | Per cent. |
|---|---|
| Wheat I | 30.94 |
| Wheat II | 30.36 |
| Wheat flour I | 46.19 |
| Wheat flour II | 34.04 |
| Maize | 42.50 |
| Sugar beet( Fresh) | 0.00 |
| Hay | 7.49 |
| Bread (Whole wheat I) | 27.93 |
| Bread (Whole wheat II) | 27.08 |
| Bread (Wheat flour I) | 39.70 |
| Bread (Wheat flour II) | 31.99 |
| Corn cake (Maize) | 40.37 |

### 4. ESTIMATION OF THE PENTOSANS AND HEMICELLULOSES BY DILUTE ACIDS.

After removing the more easily soluble constituents of the material as already described, there remains the somewhat insoluble substance incorporated in the cell walls and intimately associated with the true cellulose.

This woody or fibrous material is very far however from possessing a homogenous character, but consists of some of the most complex and least understood of the carbohydrate group, as well as some substances which cannot be regarded as carbohydrates at all.

Tollens regards the lignified cells as composed of three general classes of substances: cellulose, wood gum or pentosans, and bodies belonging undoubtedly to the aromatic group. This last is of non-carbohydrate nature. Of the first two, cellulose may be regarded as resistant to any of the reagents here proposed, while the wood gum or pentosan is easily hydrolyzed by dilute acids. In many materials other substances similar to the pentosans will occur, as for instance, galactan, mannan, dextran, even of substances of the nature of pectin, but all these behave like the pentosans to hydrolytic agents and yield specific sugars. Recent researches by Cross and Bevan throw much light upon the constitution of these non-cellulose materials. The hydrolyzable portions seem to be largely of the nature of pentosans or their derivatives.[1] The most rational treatment of the material at this stage would therefore seem to be such as would dissolve this group of similar substances and convert them into a form capable of ready estimation. For this purpose, treatment with dilute hydrochloric acid has been found preferable to any other.

The reagent was selected because, as shown by Councler,[2] it possesses superior hydrolytic power to sulphuric acid towards these very substances. Repeated use of hydrochloric acid in this laboratory for the purposes of hydrolyzing large quantities of gums and similar materials has shown that its action is quicker and that fewer by-products result than when sulphuric acid is used.

A recent paper by Cross, Bevan and Smith,[3] suggests the use of one per cent. sulphuric acid for this purpose, and heating in an autoclave during thirty minutes at a pressure of three atmospheres. Their results do not indicate a greater degree of efficiency than the method here presented, while the operation would prove less convenient for many analysts.

With regard to the duration of treatment and the strength of

1 *Chem. News*, 74. 175; *Ber. d. chem. Ges.*, 29. 1457.
2 *Chem. Ztg.*, 16. 1719.
3 *Ber. d. chem. Ges.*, 29, 1457.

acid to be employed, a systematic study has indicated that one hour's boiling under a reflux condenser with 100 cc. of one per cent. hydrochloric acid, gave the most satisfactory results. The accuracy of this conclusion was determined by ascertaining the conditions which yielded the largest amount of reducing sugar without appreciably diminishing the amount of crude fiber obtained at the close of the analysis, it being thought undesirable to increase the intensity of this reaction at the expense of the fiber. After one hour's boiling with the acid of the concentration mentioned, there remains in the material only very slight traces of soluble matters which could be converted into reducing sugars.[1]

In the absence of other bodies similar to the pentosans this method will undoubtedly furnish a quicker and more accurate method of determining the latter than the well known destructive distillation with strong hydrochloric acid and subsequent estimation of the furfurol thus found.

As a factor for the reducing coefficient of the sugars thus formed, that of xylose has been chosen as probably representing the most common and most abundant sugar present under these conditions (one cc. Fehling's solution requires for complete reduction 0.004617 gram of xylose.)[2]

The equivalent of xylose in xylan as originally present in the material may be estimated after the manner of finding the equivalent of dextrose in starch, according to the proportion

$$\underset{\text{xylose.}}{C_5H_{10}O_5} : \underset{\text{xylan.}}{C_5H_8O_4} :: 100 : x.$$

PENTOSANS DISSOLVED BY BOILING WITH ONE PER CENT. HYDROCHLORIC ACID.

| | Per cent. |
|---|---|
| Wheat I | 4.54 |
| Wheat II | 4.37 |
| Wheat flour I | 0.00 |
| Wheat flour II | 0.00 |
| Maize | 5.14 |
| Sugar beet (Fresh) | 4.89 |
| Hay | 7.14 |
| Bread (Whole wheat I) | 4.16 |
| Bread (Whole wheat II) | 4.34 |
| Bread (Wheat flour I) | 0.00 |
| Bread (Wheat flour II) | 0.00 |
| Corn cake (Maize) | 3.54 |

[1] Cross, Bevan and Beadle, This Journal, **18**, 8, state that the residue from a successive treatment by boiling alcohol, dilute sodium hydroxide, and dilute hydrochloric acid is free from pentosans and all the more readily hydrolyzable constituents.

[2] *Am. Chem. J.*, **13**, 73.

### 5. ESTIMATION OF CRUDE FIBER.

The residue from the preceding treatment still contains in addition to the actual fiber or cellulose a considerable amount of a substance not hydrolyzable to reducing sugars, by means of dilute acids, but which is readily soluble in dilute alkalies. This frequently forms a considerable proportion of the nitrogen-free extract. Repeated treatment of such alkaline solutions with dilute acids (after neutralizing the alkali) have failed to produce any considerable amount of reducing sugars. An investigation of the nature of this substance is now in progress, but there seems little ground at this time for regarding it as of the nature of a carbohydrate. It probably deserves separate classification as non-nitrogenous and non-carbohydrate in its nature.

The residue from treatment with dilute acid is therefore boiled under a reflux condenser for thirty minutes with 200 cc. of 1.25 per cent. sodium hydroxide, filtered, washed, dried, weighed, and ignited in the manner prescribed for the ordinary estimation of crude fiber.

Following are the results obtained in this way :

CRUDE FIBER RESULTING AFTER TREATMENT WITH BOILING ALCOHOL, COLD WATER, MALT EXTRACT, BOILING ONE PER CENT. HYDROCHLORIC ACID AND BOILING ONE AND ONE-FOURTH PER CENT. SODIUM HYDROXIDE.

| | Per cent. |
|---|---|
| Wheat I | 2.68 |
| Wheat II | 2.51 |
| Wheat flour I | 0.25 |
| Wheat flour II | 0.25 |
| Maize | 1.99 |
| Sugar beet (Fresh) | 1.00 |
| Hay | 34.34 |
| Bread (Whole wheat I) | 2.70 |
| Bread (Whole wheat II) | 2.02 |
| Bread (Wheat flour I) | 0.34 |
| Bread (Wheat flour II) | 0.17 |
| Corn cake (Maize) | 2.22 |

The percentage of crude fiber obtained in this way will not be essentially different from the results obtained by the Weender method.

A better comprehension of the significance of these results

will be had from their collective presentation in the following table. From this it will be seen that in each material six, or in some cases, seven forms of carbohydrates have been quantitatively determined, the results showing at a glance the comparative value of the material for use either as a food or for technical purposes, as no other existent method of analysis could do. The sum of these various items constitute of course the total carbohydrates in the respective materials.

TABLE SHOWING THE RESPECTIVE PERCENTAGES OF DIFFERENT CARBOHYDRATES IN CERTAIN FOOD-STUFFS.

| Material analyzed. | Sucrose. Per cent. | Invert sugar. Per cent. | Dextrin. Per cent. | Soluble starch. Per cent. | Normal starch. Per cent. | Pentosans. Per cent. | Crude fiber. Per cent. |
|---|---|---|---|---|---|---|---|
| Wheat I..... | 0.52 | 0.08 | 0.27 | 0.00 | 30.94 | 4.54 | 2.68 |
| Wheat II..... | 0.72 | 0.00 | 0.41 | 0.00 | 30.36 | 4.37 | 2.51 |
| Wheat flour I..... | 0.18 | 0.00 | 0.90 | 0.00 | 46.19 | 0.00 | 0.25 |
| Wheat flour II..... | 0.20 | 0.00 | 1.06 | 0.00 | 34.04 | 0.00 | 0.25 |
| Maize ..... | 9.27 | 0.00 | 0.32 | 0.00 | 42.50 | 5.14 | 1.99 |
| Sugar beet (Fresh).... | 8.38 | 0.07 | 0.35 | 0.00 | 0.00 | 4.89 | 1.00 |
| Hay ..... | 2.53 | 0.00 | 1.18 | 0.00 | 7.49 | 7.18 | 34.34 |
| Bread (Whole wheat I) | 0.05 | 0.32 | 0.68 | 1.37 | 27.93 | 4.16 | 2.70 |
| Bread (Whole wheat II) | 0.06 | 0.37 | 0.23 | 2.36 | 27.08 | 4.34 | 2.02 |
| Bread (Wheat flour I). | 0.01 | 0.10 | 0.27 | 1.99 | 34.70 | 0.00 | 0.34 |
| Bread (Wheat flour II) | 0.15 | 0.38 | 0.91 | 1.74 | 31.99 | 0.00 | 0.17 |
| Corn cake (Maize).... | 0.16 | 0.19 | 0.00 | 2.80 | 40.37 | 3.54 | 2.22 |

In many cases it is believed that the total amount of carbohydrates thus definitely determined in food materials will be found to be appreciably less than the nitrogen-free extract estimated by difference. If subsequent research should justify this belief, the character of this non-carbohydrate and non-nitrogenous substance would remain to be determined. This question is now being investigated and for the present the writer desires to reserve the subject of inquiry to this laboratory.

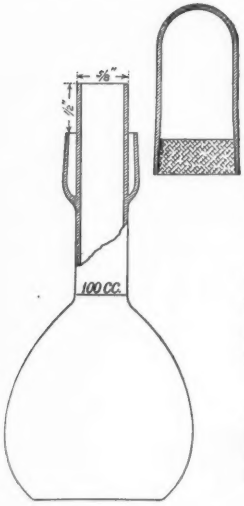
This outline is thought to present an analytical method superior to anything at present available for the estimation of carbohydrates in foods, although it cannot be regarded as in any sense perfected. It will have served its purpose if it shall suggest to others the necessity of something better and assist them in the search for it.

## A NEW CALIBRATED WEIGHING FLASK.

By George L. Heath.

Received January 8, 1897.

A FLASK has been designed by the writer which possesses some advantages over the ordinary graduated flasks in use. From the designs, Eimer and Amend, of New York, make very neat flasks, which may be illustrated by the accompanying diagram.




The drawing shows the upper part of the neck, as if half cut away, giving a sectional view of the stem, and annular cup surrounding it.

The outside of the cup is ground to fit the light glass cap which slips over it. (See sectional view of cap.)

The flask is especially adapted to weighing liquids, as, for instance, portions of standard ferric chloride solutions for titrations as recommended in Blair's Iron Analysis.

The solution may be kept some time without any change in weight, since the joint of cup and cap is as tight as in other glass stoppered bottles.

A little vaseline may be used, for the cap never comes in contact with the solution like an ordinary stopper.

This form of stopper cannot cement to the flask. After weighing and then mixing some solution, a portion may be poured off, and the little annular cup will retain any drop that might drip over the edge in pouring, and the cap, immediately replaced, prevents evaporation till the flask and remaining contents can be weighed.

In selecting ordinary graduated flasks to be fitted with such an annular cup and glass cap, those are preferably taken which have rather narrow necks, for the graduation of such is a little more accurate, and the cap, etc., may be smaller and neater in appearance, especially when applied to a large sized vessel.

The moderate expense necessary to fit flasks in this manner is the only disadvantage we have noted.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

# THE VELOCITY OF THE REACTION BETWEEN FERROUS CHLORIDE, POTASSIUM CHLORATE AND HYDROCHLORIC ACID.

BY A. A. NOYES AND R. S. WASON.

Received January 12, 1897.

## I. PURPOSE OF THE INVESTIGATION.

THE velocity of the reaction between ferrous sulphate, potassium chlorate, and sulphuric acid was investigated many years ago by J. J. Hood.[1] The results of his experiments are briefly as follows: In the presence of an undetermined excess of sulphuric acid, the velocity of the reaction at any moment was found to be directly proportional, throughout each separate series of experiments, to the product of the concentrations of the ferrous sulphate and potassium chlorate. This was proved to be true not only in the series where these two substances were originally present in equivalent amounts, but also in those where one or the other of the two substances was present in excess. The author states, without presenting experimental results, that the same law was found to govern the reaction between ferrous chloride, potassium chlorate, and hydrochloric acid. He also studied the effect of acid on the former reaction, and showed that its velocity increased more rapidly than the increase in the concentration of the acid. He determined, furthermore, the relative influence of sulphuric and hydrochloric acids on the rate of the reaction, and also the effect of varying the temperature between the limits of 10° and 32°.

We have undertaken the investigation of the very similar reaction referred to in the title of this article with several objects in view: First, in order to confirm Hood's conclusion that the reaction is one of the second order with respect to the ferrous salt and the chlorate, by the far more reliable method[2] of varying the initial concentration and comparing the velocity constants of the different series. Second, in order to determine more definitely the influence of acid, especially hydrochloric acid, on the speed of the reaction: if found proportional to the concentration of the acid, the result would be of interest as furnishing a new

[1] *Phil. Mag.* (5), 6, 371; 8, 121; 20, 323.

[2] See Noyes: *Zischr. phys. Chem.*, 18, 118.

example of a third order reaction; if not proportional, the velocity might prove, like that of the reaction between hydriodic and bromic acids,[1] to be proportional to the square or some other simple power of the concentration of the hydrogen ions. Third, in order to investigate within wider limits the effect of temperature on the velocity of the reaction, with a view of further confirming the remarkable laws which have lately been discovered in regard to the relation between temperature and reaction-velocity.

It seemed desirable, moreover, to undertake this investigation in spite of the extended experiments of Hood on the analogous sulphate reaction, by reason of the fact that, according to the Electrolytic Dissociation Theory, the molecular composition of the dissolved substances is much simpler in the case of the chlorides than in that of the sulphates; namely, at the concentration used in these experiments, hydrochloric acid is nearly completely dissociated, while sulphuric acid is dissociated only to a moderate extent, so that its degree of dissociation varies considerably with its concentration, which is therefore not proportional to the concentration of the hydrogen ions. Furthermore, ferrous sulphate is less dissociated than ferrous chloride; and ferric sulphate, which is a product of the reaction, is hydrolyzed to a greater extent than the corresponding chloride. A closer correspondence of the experimental results with simple empirical and theoretical formulas is therefore to be expected in the case of the chloride.

## 2. THE EXPERIMENTAL METHOD OF PROCEDURE.

The standard stock solutions employed in our investigation were a half-normal solution of ferrous chloride and one of potassium chlorate, a normal solution of hydrochloric acid, and an approximately tenth-normal solution of potassium permanganate.[1] The ferrous chloride solution was prepared by boiling strong hydrochloric acid with a large excess of pure iron wire, with a return cooler, as long as any action took place; the solution was then diluted until it became exactly half-normal, a standard potassium bichromate solution being used for this purpose. The

[1] Noyes: *Ztschr. phys. chem.*, 19, 599.

[2] The word normal is used throughout this article with reference to the oxidizing power of the substance.

ferrous chloride solution was kept under a pressure of carbon dioxide, in order to prevent its oxidation. A chlorine determination made in it showed that it was almost perfectly neutral. The half-normal potassium chlorate solution was made by dissolving 10.21 grams of the recrystallized commercial salt in one liter of water. The hydrochloric acid solution was prepared by diluting the chemically pure acid, pure calcium carbonate being used for its standardization. The permanganate solution used was standardized against the ferrous chloride solution, and was found to be 0.1011 normal; 25.00 cc. of the ferrous solution, measured after it was diluted to a tenth-normal concentration, therefore required 24.72 cc. of this permanganate solution.

In carrying out the velocity experiments, a mixture of the reacting substances consisting of 250 or 500 cc. was made up by means of pipettes from the stock solutions and from freshly boiled distilled water in glass-stoppered bottles from which the air had been displaced by carbon dioxide. The appropriate amounts of water, ferrous chloride solution, and hydrochloric acid, were first placed in the bottles, which were then put into a large water thermostat provided with an efficient stirrer. After the mixture had attained the temperature of the bath, the proper amount (50 or 100 cc.) of the chlorate solution previously brought to the same temperature, was added from a rapidly delivering pipette, the time noted, and the mixture instantly shaken. After suitable intervals, portions of twenty-five or fifty cc. were removed, and run into 200–300 cc. of cold, boiled water containing about one gram of manganous sulphate and small quantities of sulphuric acid and sodium phosphate; this solution was then immediately titrated with the permanganate. It is known[1] that under these conditions the permanganate process furnishes accurate results, even though chlorides are present; and in our own experiments no difficulty was found in getting a sharp end-point.

The temperature of the thermostat was kept constant in all cases within 0.1° C., and was 20° unless otherwise mentioned.

### 3. EXPERIMENTAL RESULTS ON THE EFFECT OF THE CONCENTRATION OF THE REACTING SUBSTANCES.

The three reacting substances were brought together in nine

[1] Zimmermann: *Ber. d. chem. Ges.*, **14**, 779; Reinhardt: *Chem. Ztg.*, **13**, 323; Mixer and DuBois: This Journal, **17**, 406.

different proportions, in order to establish with certainty the order of the reaction, and to show the effect of each substance separately on its velocity. In the first five series the concentrations of the ferrous chloride and potassium chlorate were kept constant, and that of the hydrochloric was varied. In five of the series, on the other hand, the amount of acid present was constant, and the concentrations of the other two substances were variable.

Check determinations were made in every case. The results of all these experiments are presented in the table below. The values in the column headed $t$ are the times in minutes counted from the moment of mixing. Those in the columns headed $x_1$ and $x_2$ are the number of cubic centimeters of the permanganate solution corresponding to the amount of ferrous salt already oxidized at the time $t$ in the two duplicate experiments. The values of $x$ are the means of these two quantities. The values of $A-x$ represent the number of cubic centimeters corresponding to the unoxidized ferrous salt present at the time $t$. The initial value of ferrous salt in terms of the permanganate—that is, the value of $A$ — is 24.72 in all the series except Nos. 7 and 9, and 49.44 in the case of these two series.[1] The columns headed $10^6C_2$ and $10^7C_3$ contain the calculated values of the velocity-constants of the second and third orders respectively. The values of $C_2$ are those of the constant in the differential equation:

$$\frac{dx}{dt} = C_2(A-x)(B-x),$$

where $A$ and $B$ represent the initial quantities of ferrous chloride and potassium chlorate, and $x$ the amount changed over at the time $t$, and where the variation in the concentration of the hydrochloric acid is disregarded. The values of $C_3$ are those of the constant in the equation:

$$\frac{dx}{dt} = C_3(A-x)(B-x)(C-x),$$

which states that the velocity of the reaction is directly proportional to the concentration of each of the three reacting substances. For the integrated forms of this equation by which the numerical calculations were made in the different cases, we refer

[1] For twenty-five cc. of the reaction-mixture were titrated in series Nos. 1 to 5, and in No. 9, and fifty cc. in the other series (Nos. 6 to 8).

to the article of Fuhrmann.[1] All of these constants are expressed in the same arbitrary units, those corresponding to the number of cubic centimeters of permanganate required for the titration. If the values of $A$, $B$, $C$, and $x$ were expressed in gram-equivalents per liter, the values of $C_2$ would be 247.2 times, and the values of $C_3$ 61120 times as great as those here given. We mention this fact, for we think it unfortunate that authors in presenting the results of investigations on the velocity of reactions so often neglect to determine, or at any rate to state, the factor by which their arbitrary reaction-constants can be reduced to an absolute standard.

TABLE I.

| Series No. | Normal concentration of $FeCl_2$. | $KClO_3$. | HCl. | $t$. | $x_1$. | $x_2$. | $x$. | $A-x$. | $10^6C_2$. | $10^7C_3$. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.1 | 0.1 | 0.0 | 15 | 0.00 | 0.00 | 0.00 | 24.72 | ... | ... |
| | | | | 45 | 0.03 | 0.01 | 0.02 | 24.70 | ... | ... |
| | | | | 100 | 0.08 | 0.05 | 0.06 | 24.66 | ... | ... |
| | | | | 250 | 0.55 | 0.48 | 0.51 | 24.21 | ... | ... |
| 2 | 0.1 | 0.1 | 0.1 | 5 | 1.22 | 1.14 | 1.19 | 23.53 | 408 | 171 |
| | | | | 15 | 3.04 | 3.00 | 3.02 | 21.70 | 375 | 162 |
| | | | | 35 | 5.79 | 5.97 | 5.88 | 18.85 | 360 | 168 |
| | | | | 60 | 8.24 | 7.97 | 8.12 | 16.60 | 331 | 166 |
| | | | | 110 | 11.26 | 11.07 | 11.17 | 13.55 | 303 | 173 |
| | | | | 170 | 13.05 | 12.96 | 12.98 | 11.74 | 264 | 165 |
| 3 | 0.1 | 0.1 | 0.2 | 5 | 2.50 | 2.42 | 2.46 | 22.28 | 886 | 189 |
| | | | | 15 | 5.42 | 5.40 | 5.41 | 19.31 | 756 | 162 |
| | | | | 35 | 9.60 | 9.82 | 9.70 | 15.08 | 746 | 171 |
| | | | | 60 | 12.25 | 12.35 | 12.30 | 12.40 | 670 | 160 |
| | | | | 107 | 15.27 | 15.40 | 15.32 | 9.40 | 616 | 158 |
| | | | | 167 | 17.54 | 17.67 | 17.62 | 7.10 | 600 | 136 |
| 4 | 0.1 | 0.1 | 0.3 | 5 | 3.37 | 3.22 | 3.32 | 21.40 | 1250 | 174 |
| | | | | 12 | 6.57 | 6.42 | 6.49 | 18.23 | 1200 | 170 |
| | | | | 22 | 9.56 | 9.47 | 9.52 | 15.20 | 1150 | 168 |
| | | | | 35 | 12.27 | 12.22 | 12.25 | 12.47 | 1130 | 174 |
| | | | | 55 | 14.47 | 14.60 | 14.54 | 10.18 | 1050 | 177 |
| | | | | 85 | 16.97 | 16.97 | 16.97 | 7.75 | 1030 | 166 |
| 5 | 0.1 | 0.1 | 0.5 | 1 | 1.20 | 1.12 | 1.16 | 23.56 | 2000 | 163 |
| | | | | 3 | 3.44 | 3.52 | 3.48 | 21.24 | 2210 | 181 |
| | | | | 7 | 7.00 | 6.92 | 6.96 | 17.76 | 2240 | 189 |
| | | | | 12 | 9.72 | 9.72 | 9.72 | 15.00 | 2180 | 185 |
| | | | | 22 | 13.28 | 13.22 | 13.24 | 11.48 | 2120 | 185 |
| | | | | 37 | 16.10 | 16.14 | 16.12 | 8.60 | 2050 | 182 |

[1] *Ztschr. phys. Chem.*, 4, 89.

| Series No. | Normal concentration of $FeCl_2$. | of $KClO_3$. | HCl. | $t$. | $x_1$. | $x_2$. | $x$. | $A-x$. | $10^6C_2$. | $10^7C_3$. |
|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 0.05 | 0.05 | 0.2 | 5 | 1.12 | 1.08 | 1.10 | 23.62 | 708 | 153 |
| | | | | 15 | 3.22 | 3.14 | 3.18 | 21.54 | 796 | 164 |
| | | | | 50 | 7.97 | 8.10 | 8.02 | 16.70 | 776 | 165 |
| | | | | 100 | 11.84 | 11.89 | 11.86 | 12.86 | 768 | 162 |
| | | | | 160 | 14.62 | 14.67 | 14.65 | 10.07 | 738 | 165 |
| | | | | 250 | 16.82 | 16.97 | 16.90 | 7.82 | 700 | 160 |
| 7 | 0.1 | 0.05 | 0.2 | 5 | 2.14 | 2.49 | 2.30 | 47.14 | 788 | 157 |
| | | | | 12 | 4.72 | 4.87 | 4.30 | 44.64 | 790 | 160 |
| | | | | 40 | 11.81 | 11.64 | 11.74 | 37.70 | 744 | 164 |
| | | | | 70 | 15.54 | 15.51 | 15.53 | 33.91 | 708 | 161 |
| | | | | 110 | 18.44 | 18.52 | 18.49 | 30.95 | 668 | 154 |
| | | | | 170 | 21.10 | 20.94 | 21.04 | 28.40 | 642 | 149 |
| 8 | 0.05 | 0.1 | 0.2 | 5 | 2.02 | 2.27 | 2.17 | 22.55 | 762 | 161 |
| | | | | 12 | 4.92 | 5.07 | 5.00 | 19.72 | 804 | 166 |
| | | | | 22 | 8.02 | 8.10 | 8.07 | 16.65 | 798 | 169 |
| | | | | 40 | 11.92 | 11.92 | 11.92 | 12.80 | 762 | 168 |
| | | | | 70 | 15.92 | 15.86 | 15.89 | 8.83 | 740 | 160 |
| | | | | 110 | 18.82 | 18.87 | 18.82 | 5.90 | 700 | 162 |
| 9 | 0.2 | 0.2 | 0.2 | 1 | 1.94 | 1.94 | 1.94 | 47.50 | 830 | 170 |
| | | | | 2 | 3.72 | 3.76 | 3.74 | 45.70 | 830 | 175 |
| | | | | 4 | 6.71 | 6.77 | 6.74 | 42.70 | 800 | 174 |
| | | | | 7 | 10.29 | 10.24 | 10.26 | 39.20 | 749 | 170 |
| | | | | 15 | 16.49 | 16.71 | 16.61 | 32.83 | 682 | 173 |
| | | | | 25 | 21.32 | 21.26 | 21.29 | 28.15 | 612 | 170 |

## 4. DISCUSSION OF THE RESULTS ON THE EFFECT OF THE CONCENTRATION OF THE REACTING SUBSTANCES.

The first series of experiments presented above clearly shows that in neutral solution the reaction does not take place to an appreciable extent. The very slight decrease in the concentration of the ferrous salt, amounting only to a quarter of a per cent. in 100 minutes and to two per cent. in 250 minutes, may well be due to oxidation by the air or to the presence of a small quantity of acid in the ferrous chloride solution.

Attention may next be directed to the fact that, in the experiments in which the acid was present in large excess, especially in Series No. 5, the values of $C_2$ are nearly constant, thus confirming Hood's conclusion that the velocity of the reaction under such circumstances is directly proportional to the product of the concentrations of the ferrous salt and of the chlorate.

The order of the reaction and the effect of each substance on

its velocity, is, however, best determined by applying to the results as a whole the two distinct methods available for this purpose.

The first of these methods is the one most commonly employed. It consists in determining which order of constants shows the smallest variations throughout each *separate* series of experiments. Now, a brief inspection of the foregoing table suffices to show that, in all the series except those where a large excess of the acid was present, the values of $C_2$ show a continuous decrease as the reaction progresses; that the value of $C_3$, on the other hand, in every case remains practically constant, or exhibits only irregular variations plainly arising from experimental errors. Judged by this method, the reaction is therefore one of the third order.

The second method of determining the order of reactions was first employed by van't Hoff,[1] and its importance was later emphasized by the experiments of Noyes and Scott.[2] In the form used by the latter investigators it consists in determining which order of constants has most nearly the same value in independent series of experiments in which the initial concentrations are made widely different from one another. This method is much more reliable than the first one by reason of the fact that the influence of disturbing causes, such as the effect of the products of the reaction on its velocity, becomes insignificant in comparison with the much greater effect of the large changes in the initial concentrations. In order to show more clearly the result of the application of this second method to the reaction here considered, we have prepared the following table, in which are brought together the comparable values of the two orders of constants derived from the eight series of experiments; namely, the mean values of $C_3$ and the values of $C_2$ corresponding to that stage of the reaction at which one-half of the iron is oxidized.

TABLE II.

| Series No. | Normal concentration of $FeCl_2$. | $KClO_3$. | HCl. | $10^6 C_2$. | $10^7 C_3$. |
|---|---|---|---|---|---|
| 2 | 0.1 | 0.1 | 0.1 | 243 | 168 |
| 3 | 0.1 | 0.1 | 0.2 | 670 | 163 |
| 4 | 0.1 | 0.1 | 0.3 | 1130 | 172 |
| 5 | 0.1 | 0.1 | 0.5 | 2130 | 184 |
| 6 | 0.05 | 0.05 | 0.2 | 763 | 163 |
| 7 | 0.1 | 0.05 | 0.2 | 739 | 157 |
| 8 | 0.05 | 0.1 | 0.2 | 760 | 164 |
| 9 | 0.2 | 0.2 | 0.2 | 727 | 172 |

[1] Etudes de dynamique chimique. [2] *Ztschr. phys. Chem.*, 18, 118.

It is seen that the values of $C_3$ are approximately the same in all eight series of experiments, conclusively proving that the reaction is one of the third order, and that its velocity is proportional to the concentration of each of the reacting substances. The values of $C_2$ increase as the concentration of the acid increases, but are, like those of $C_3$, approximately constant in the last four series of experiments, in all of which the same excess of acid was present, showing that the reaction is one of the second order in the presence of an excess of acid.

These experiments furnish the first satisfactory example of a reaction of the third order in which three distinct substances are involved.

It is worth while to consider briefly the question of the theoretical significance of the fact that this reaction is one of the third order. The following equation expresses the change which, according to the Electrolytic Dissociation Theory, takes place in the molecular composition of the substances in solution:

$$6\overset{++}{Fe} + 6\overset{+}{H} + \overset{-}{ClO_3} = 6\overset{+++}{Fe} + \overset{-}{Cl} + 3H_2O.$$

It is seen that no less than thirteen molecules are involved in this reaction. It is, however, highly probable that the reduction of the chlorate takes place in three separate stages, and that it is only the first one of these which requires an appreciable time for its completion;[1] in which case the reaction whose velocity is measured would be the following one:

$$2\overset{++}{Fe} + 2\overset{+}{H} + \overset{-}{ClO_3} = 2\overset{+++}{Fe} + \overset{-}{ClO_2} + H_2O.$$

But even in this reaction five molecules participate; and it would, therefore, be expected, in accordance with kinetic and thermo-dynamical considerations, that the reaction would be one of the fifth order, or one of the third order in presence of the excess of acid.

The only kinetic explanation of the actual order of the reaction that we are able to suggest is that the ferrous ions are diatomic (namely of the formula $[\overset{++++}{Fe_2}]$, and that the hydrogen ions in the first instance act catalytically. The reaction whose velocity is measured would then be: $[\overset{++++}{Fe_2}] + \overset{-}{ClO_3} = [\overset{++++}{Fe_2O}] + \overset{-}{ClO_2}$, or $[\overset{++++}{Fe_2}] + \overset{-}{ClO_3} + H_2O = 2\overset{+}{Fe}\overset{+}{OH} + \overset{-}{ClO_3}$, the basic ferric ion

[1] Compare Noyes: *Ztschr. phys. Chem.*, 19, 599.

($[\overset{++++}{Fe_2}O]$ or $\overset{+}{Fe}\overset{+}{O}H$) being subsequently instantaneously neutralized by the acid. But, in the absence of confirmatory evidence, very little weight can be attached to such a hypothesis, and it must be admitted that, apparently at least, the reaction forms an exception to van't Hoff's principle, which states that the order of a reaction is determined by the number of molecules taking part in it.

5. EXPERIMENTAL RESULTS ON THE EFFECT OF TEMPERATURE.

It is very desirable that the interesting conclusions which have been drawn from recent investigations on the effect of temperature on the velocity of reactions should be confirmed within wider limits of temperature and by the study of new reactions. Since no experiments had been made in this direction on the reaction between ferrous chloride, potassium chlorate, and hydrochloric acid, and since the experiments of Hood on the analogous sulphate reaction were confined to the range of temperature between 10° and 32°, we have measured the velocity of the former reaction at six different temperatures varying uniformly (by differences of 10°) between 0° and 50°. Owing to small variations in the temperature of the thermostat, the series at 30° and 50° are unfortunately less accurate than those of Table I.

The results are contained in the following table. The headings have the same significance as before. The concentration of the solution was in all six cases the same; namely, one-tenth normal with reference to each of three reacting substances.

TABLE III.

| Series No. | Temperature. | $t$. | $x_1$. | $x_2$. | $x$. | $A-x$. | $10^6C_2$. | $10^7C_3$. |
|---|---|---|---|---|---|---|---|---|
| 10 | 0° | 5 | 0.20 | 0.15 | 0.18 | 24.73 | 56.0 | 21.0 |
| | | 20 | 0.70 | 0.62 | 0.65 | 24.25 | 54.0 | 21.5 |
| | | 40 | 1.38 | 1.32 | 1.35 | 23.55 | 57.4 | 23.4 |
| | | 100 | 2.95 | 2.98 | 2.96 | 21.94 | 53.9 | 22.9 |
| | | 195 | 4.81 | 4.97 | 4.90 | 20.00 | 50.9 | 22.7 |
| 11 | 10° | 5 | 0.58 | 0.55 | 0.57 | 24.33 | 188 | 76.2 |
| | | 20 | 1.70 | 1.72 | 1.70 | 23.20 | 148 | 61.0 |
| | | 50 | 3.60 | 3.70 | 3.65 | 21.25 | 138 | 60.0 |
| | | 100 | 6.34 | 6.17 | 6.25 | 18.65 | 134 | 63.0 |
| | | 160 | 8.37 | 8.40 | 8.38 | 16.52 | 126 | 64.0 |
| | | 250 | 10.52 | 10.47 | 10.50 | 14.40 | 117 | 64.0 |
| 12 | 20° | See Series 2, Table I. | | | | | | |

| Series No. | Temperature. | $t$. | $x_1$. | $x_2$. | $x$. | $A-x$. | $10^6C_2$. | $10^7C_3$. |
|---|---|---|---|---|---|---|---|---|
| 12 | 30° | 5 | 2.45 | 2.35 | 2.40 | 22.50 | 856 | 357 |
| | | 10 | 4.50 | 4.55 | 4.52 | 20.38 | 891 | 387 |
| | | 18 | 6.70 | 6.72 | 6.70 | 18.20 | 821 | 390 |
| | | 32 | 9.52 | 9.50 | 9.50 | 15.40 | 774 | 406 |
| | | 55 | 12.07 | 12.05 | 12.06 | 12.84 | 703 | 404 |
| | | 95 | 14.65 | 14.70 | 14.68 | 10.22 | 606 | 418 |
| 13 | 40° | 5 | 5.30 | 5.15 | 5.22 | 19.68 | 2130 | 971 |
| | | 9 | 7.57 | 7.61 | 7.59 | 17.31 | 1950 | 954 |
| | | 16 | 10.50 | 10.42 | 10.46 | 14.44 | 1810 | 992 |
| | | 30 | 13.40 | 13.59 | 13.50 | 11.40 | 1580 | 1010 |
| | | 50 | 15.65 | 15.60 | 15.62 | 9.28 | 1350 | 990 |
| | | 80 | 17.48 | 17.50 | 17.49 | 7.41 | 1180 | 1030 |
| 14 | 50° | 1 | 2.55 | 2.40 | 2.48 | 22.42 | 4440 | 1970 |
| | | 3 | 6.18 | 6.25 | 6.22 | 18.68 | 4480 | 2050 |
| | | 6 | 9.55 | 9.38 | 9.46 | 15.44 | 4100 | 2140 |
| | | 11 | 12.62 | 12.65 | 12.64 | 12.26 | 3760 | 2290 |
| | | 20 | 15.38 | 15.42 | 15.40 | 9.50 | 3250 | 2370 |
| | | 30 | 17.00 | 16.97 | 16.98 | 7.92 | 2150 | 2390 |

## 6. DISCUSSION OF THE RESULTS ON THE EFFECT OF TEMPERATURE.

As was first shown by van't Hoff,[1] it follows from the laws of thermodynamics that the following relation must exist between the absolute temperature $T$, the heat effect $q$ accompanying the reaction, and the velocity-constants, $k'$ and $k''$, of the two opposing reactions which are considered to be in equilibrium with one another:

$$\frac{d\log_e k'}{dT} - \frac{d\log_e k''}{dT} = \frac{q}{2T^2}.$$

Van't Hoff adds that, although this equation does not give the desired relation between temperature and the velocity constants of the *separate* reactions, it shows nevertheless that the relation has the following form:

$$\frac{d\log_e k}{dT} = \frac{A}{T^2} + B.$$

It is to be noted, moreover, that in this equation $A$ is a quantity which, like $q$ in the preceding one, will, in general, probably vary but little with the temperature, and that $B$ is a quantity which must have the same numerical value for the two opposed

1 Etudes de dynamique chimique, p. 115.

reactions at any temperature at which they may be compared, for only in that case would this term disappear in the preceding equilibrium equation. This fact in regard to the quantity $B$ makes it seem probable that its value is zero. At any rate, this is the simplest assumption that can be made in regard to it, and the one whose validity it is first natural to test by a comparison with the facts. Integrating then the differential equation between the limits $T_1$ and $T_2$ (to which correspond the velocity constants $k_1$ and $k_2$), under the assumptions that $B = 0$, and that $A$ does not vary with the temperature, we get:

$$\log_e \frac{k_1}{k_2} = \frac{T_1 - T_2}{T_1 T_2}.$$

Now, it has been shown by Arrhenius[1] that this equation does in fact satisfactorily represent the relation between temperature and velocity-constants in the case of five different reactions. In the case of two other reactions considerable deviations from the formula were found to exist, but these were attributed to experimental errors arising from the high temperatures employed.

In order to determine whether our results are in accord with this formula, we have calculated the ratios ($k_1 : k_2$) of the mean values of $C_3$ for each successive pair of temperatures, and from these ratios we have calculated the constant $A$ in the above equation, and have brought the results together in the following table:

TABLE IV.

| Series No. | Temperature. | $10^7 C_3$ or $k$. | $k_1 : k_2$. | $A$. |
|---|---|---|---|---|
| 10 | 0 | 22.7 | 2.75 | 7820 |
| 11 | 10 | 62.4 | 2.68 | 8180 |
| 12 | 20 | 167.0 | 2.36 | 7620 |
| 13 | 30 | 394.0 | 2.52 | 8760 |
| 14 | 40 | 992.0 | 2.22 | 8070 |
| 15 | 50 | 2200.0 | ... | .... |

It will be seen that the values of $A$ show only irregular variations, not a progressive one, and therefore the equation is correct within the experimental error. It is to be noted that the simpler equation:

$$\log_e \frac{k_1}{k_2} = B(T_1 - T_2)$$

(where $B$ is a constant) corresponding to the relation ($k = ab^t$)

[1] *Ztschr. phys. Chem.*, 4, 226.

employed by Berthelot in connection with his esterification experiments, would be a less satisfactory expression of the results; for this equation would require that the values of the ratios $k_1 : k_2$ should be constant at all temperatures, instead of slowly decreasing with rising temperature, as the previous equation required, as is in fact the case.

Another remarkable conclusion to which the study of the effect of temperature on the velocity of reactions has led, is that temperature apparently accelerates all chemical changes in approximately the same ratio. In other words, the values of the ratios $k_1 : k_2$ for equal differences of temperature are of the same order of magnitude for all the various reactions investigated, although these reactions differ from one another in character as widely as possible. For a ten-degree interval the average value of $k_1 : k_2$ is about 2.8, the separate values varying from 2.0 to 3.6.[1] We wish now only to call attention to the fact that the reaction here considered is another example of this principle, the value of the ratio $k_1 : k_2$ being about 2.7 for the two lower temperature-intervals.

## 7. SUMMARY.

This investigation has proved that the reaction between ferrous chloride, potassium chlorate, and hydrochloric acid is a reaction of the third order, its velocity being directly proportional to the concentration of each of the three substances. This conclusion is based not only on a consideration of the variations of the constants of the individual series, but also on the far more reliable comparison of the constants of different series of experiments made with varied initial concentrations.

It has also been proved that the effect of temperature on its velocity is expressed by van't Hoff's theoretical equation:

$$\frac{T_1 T_2}{T_1 - T_2} \log_e \frac{k_1}{k_2} = A \text{ (a constant)},$$

a formula whose applicability to several reactions had already been demonstrated by Arrhenius.

Finally, our experiments have shown that this reaction furnishes another confirmation of the empirical principle that the influence of temperature on the velocity of all reactions is of the same order of magnitude.

[1] For a summary of the results, see van't Hoff-Cohen: Studien zur chemischen Dynamik, p. 129.

DISCUSSION.

*Mr. Hazen:* There is a question, different, although somewhat similar, to that presented in the paper, which has been interesting me of late; that is, the speed with which ferrous iron in waters is oxidized to the ferric state. Ferrous iron in solution in public water supplies is a very troublesome substance. In order to get rid of it, it has to be first converted into ferric iron which can be readily removed by filtration. I have made some experiments with this removal during the past year in connection with a plant for removing iron from municipal supply, installed under our advice.

After the water was aerated and had been standing in a basin for several hours, apparently every bit of the iron was in the ferrous condition, no oxidation whatever having taken place, although the water was thoroughly aerated. The effluent from the filtration of this water was entirely free from iron, and the iron removed from the water was deposited on top of the filtering sand. It was not in the upper layers of the sand but actually on top of it.

It seems to me from this that the oxidation of the iron took place practically instantaneously and at the time when the water came in contact with the surface layer of the filter. There was no oxidation up to that time, and the oxidation then must have been complete, as no iron was deposited below or came through in the effluent. I have noticed in other cases that when the oxidation takes place gradually, the removal of iron is never complete, a small quantity remaining unoxidized in solution; but if the oxidation can be brought about at once, the action is complete and every trace of the iron is removed. In the above mentioned case, the oxidation of the iron must have been due to the water coming in contact with the ferric hydroxide already oxidized and precipitated, or to the friction and agitation of the water in getting into the filter; which, of course, introduces an entirely different condition of affairs from that of quiet standing water.

*Dr. Loeb:* In the equation, as written by Dr. Noyes, there seems to me to be one little matter left out of account, and that is as to the chlorine ions from the hydrochloric acid. Of course the hydrogen is being taken away with a part of the chlorine, the

hydrogen being oxidized, but at the same time fresh chlorine is being generated by the reduction of potassium chlorate to potassium chloride, and it seems to me, therefore, that that ought to be taken into account. I want to ask whether some neutral salt had been added in this reaction, say potassium chloride in definite quantities to see whether the influence of chlorine not in the shape of acid should be taken into account. It seems to me, if it is proved that potassium chloride is of absolutely no effect, that a question would arise, whether the influence of chloric acid, or, say, $ClO_3$ as an ion as compared with Cl as an ion will produce the difference or not. The other question I want to ask is this: I see an equation, the actual ratio between zero and ten. In some experiments I have made, with the same reaction I found that at zero and at three or four degrees I was unable to produce action at all; that is, if I took the proportion given here at zero degrees I had no reaction whatever. It would be interesting to know whether Dr. Noyes obtained a reaction at zero or whether the value is obtained by extrapolation.

*Dr. Noyes:* Replying to the first question I would say that no experiments were made on the effect of potassium chloride on the velocity of the reaction; nor, as far as the reliability of the conclusions are concerned, are they necessary. For the effect of the reaction products is eliminated by the comparison of the constants of the independent series.

In regard to the experiments at zero degree, I would say that the temperature was kept at that point as nearly as possible by adding to the water in the thermostat a very considerable quantity of ice. It is probable, as is usual in such cases, that radiation raised the temperature a little above zero; I suppose it may have been one or two-tenths of a degree above zero, perhaps. But as the column of ratios shows, there was nothing at all abnormal in the results at zero degree.

*President Dudley:* It has seemed to me that the field opened here by Dr. Noyes has a very remarkable and wide extended application in the commercial process for making steel, which we hope to see this afternoon. Some years ago I had somewhat of a contest with the manufacturers over the question of the quality of the metal used for making rails. To make a

very long story short, the point I was trying to reach was to get a softer, tougher steel for rails than the steel maker wanted to make. The final answer to me was, "We cannot make a soft, tough steel as fast as we can make a hard or more brittle steel." Part of this result was due to mechanical characteristics, that is to say, the rolling of a harder, higher carbon steel is easier, since its melting-point is lower, and it softens more under heat. But, and the point I want to bring out is, the amount of the final additions, as they are called in the steel trade, that is of the spiegel and ferromanganese added at the end of the blow to remove the oxides that are formed, is considerably greater when you make a hard steel than when you make a soft steel. Now, I think it is perfectly clear that if you add to a bath of metal, after the blow is finished—which is in reality a substance containing a good deal of metallic iron and a good deal of oxide of iron—if you add say, in one case, 500 pounds of melted spiegel, and in another case 1000 pounds, the reaction will take place more rapidly in the second case. In reality therefore, the question of the speed of the reaction, which results in freeing the bath of metal from the oxide, is a very live and important question commercially, and I am only sorry to have to tell you that the steel people were a little stronger than I was, and consequently they are making steel about as they have a mind to, and getting out the oxide, we hope, but fear that they do not.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 21.]

## THE OXIDES OF TUNGSTEN.[1]

BY EN. D. DESI.

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WHILE engaged in re-determining the atomic mass of tungsten, by reduction of its trioxide in a current of hydrogen, the writer carefully observed the color changes taking place in the oxide as the temperature varied.

When studying the literature of this metal, no precise information was found about the bodies formed during the reduction, as was expected. Although a great many compounds of tungsten have been investigated, those of the metal with oxygen have

[1] From author's thesis presented to the University of Geneva, Switzerland, for the degree of Doctor in Science.

been entirely neglected. The few recorded observations relate solely to the results of qualitative experiments.

As most of the oxides of the other elements of group VI of the periodic system, as $CrO$, $Cr_3O_4$, $Cr_2O_3$, $CrO_2$, $CrO_3$; $MoO$, $Mo_2O_5$, $Mo_3O_8$, $Mo_5O_{12}$, $Mo_8O_{17}$, $MoO_3$; $UO$, $U_3O_2$, $U_4O_5$, $U_3O_4$, $U_2O_3$, $U_3O_8$, are well known and defined, the study of the oxides of tungsten was important.

The well-determined oxides of the metal are:

1. *Tungstic Acid*, $WO_3$, obtained by treating one of the minerals with aqua regia, or by treating a tungstate with an acid, or by igniting the metal in the presence of air.

2. *The Blue Oxide*, $W_2O_5 = WO_2.WO_3$, obtained by reducing the trioxide at a low temperature with hydrogen. Care must be taken not to heat above the formation of traces of water. In this way Malagutti[1] obtained a body of constant composition. It is also prepared by treating a soluble tungstate with hydrochloric acid and tin. The liquid takes on a beautiful deep blue color, due probably to the solution of the blue oxide in the hydrochloric acid.

3. *Tungsten Dioxide*, $WO_2$, a brown substance obtained by heating the trioxide to a red heat in a current of hydrogen, or by treating a soluble tungstate with hydrochloric acid and zinc. The dioxide formed in this way is very unstable; it rapidly oxidizes to tungstic acid.

As tungsten has many properties in common with the other elements of group VI, and especially with molybdenum, it should also form intermediary oxides.

Muthmann[2] has made interesting observations upon the oxides of molybdenum. He succeeded in finding definite methods for preparing them, as well as for determining their composition. In the course of the present work the writer will return to this subject.

## PREPARATION OF TUNGSTIC ACID.

Commercial tungstic acid is a product of very dubious purity, even that of the leading manufacturers, marked C. P., invariably contains molybdic acid.

It seemed to me to be of the utmost importance to use in my

[1] *Ann. Chem.* (Liebig), 9, 273.
[2] *Ann. Chem.* (Liebig), 228, 108.

researches the purest possible material, so as to be perfectly sure that the reactions obtained are due solely to tungsten.

The preparation of chemically pure tungstic acid is a long and tedious operation which need not be described here, as it has already been outlined in detail by Smith and Desi.[1]

## OXIDES OF TUNGSTEN.

### I.

Muthmann[2] obtained molybdenum dioxide ($MoO_2$) in beautiful violet crystals by heating the following mixture for several hours:

| | Grams. |
|---|---|
| Ammonium molybdate | 8 |
| Boric acid | 7 |
| Molybdic acid | 7 |
| Fused potassium carbonate | 24 |

On account of the great analogy between tungsten and molybdenum, it was thought that tungsten dioxide could be obtained by using the same method. A similar mixture was accordingly made, taking tungsten salts instead of molybdenum, and fusing in a covered platinum crucible for three hours. The result was a porous, white mass, and at the bottom of the crucible a very small quantity of a brown substance, insoluble in water or acids. When this was ignited in a porcelain crucible, with access of air, it did not change in appearance nor in weight.

The platinum crucible was badly corroded and a second experiment resulted in several holes; a nickel crucible did not fare better.

The quantity of the brown substance was too small to allow of investigating its composition.

As satisfactory results could not be obtained with metal crucibles, the experiment was tried in a smooth Battersea crucible, using the following mixture:

| | Grams. |
|---|---|
| Ammonium tungstate | 9 |
| Tungstic acid | 7 |
| Fused potassium carbonate | 21 |
| Boric acid | 7 |

This mixture was heated in a wind furnace until a quiet fusion

[1] *J. Franklin Inst.*, 139, 290.
[2] *Ann. Chem.* (Liebig), 228, 116.

set in. After thorough cooling the crucible was broken in halves; beautiful light green crystals were found, resembling ammonium chloride in structure. After a few hours exposure to the air they became white.

Treated with water they broke down into an insoluble, amorphous, white substance free from boron, and into a soluble body. The latter, when acted upon with hydrochloric acid, became yellow in color, but when heated regained its former white color. The aqueous solution was concentrated on the water-bath; during this operation a point was reached, when a very viscous liquid was obtained, which could not be evaporated to dryness. This is one of the properties of a large number of double salts of boric and tungstic acids.

Diluting this viscous liquid with a few drops of water, it was placed in a vacuum desiccator, over sulphuric acid. After a week small crystals appeared, and a little later beautiful, hexagonal, perfectly developed prisms, soluble with difficulty in water. Besides these well-developed crystals, a white, amorphous powder separated, very soluble in water. The crystals were separated from the amorphous substance, dissolved in water and the solution placed in a vacuum desiccator. This operation was repeated several times, but the white, amorphous substance appeared every time, showing that the crystalline substance had broken down into two bodies, both containing tungsten, boron, and potassium.

The object being to investigate the oxides of tungsten, the study of these two bodies was not continued any further.

## II.

### ACTION OF SULPHURIC ACID UPON METALLIC TUNGSTEN AT THE ORDINARY ATMOSPHERIC PRESSURE.

In most of our chemical treatises the statement is made that metallic tungsten is not acted upon by sulphuric acid, or at least very slightly. The writer's experience demonstrates the contrary, for metallic tungsten is readily attacked by concentrated sulphuric acid at a temperature of 200° C. It is not possible, however, to dissolve it completely, even in the boiling acid. In this respect it differs from molybdenum, which is readily dissolved in concentrated sulphuric acid far below 200° C.

Metallic tungsten and thirty-five cc. of concentrated sulphuric acid were introduced into a small flask. Sufficient heat was applied to maintain a quiet evolution of sulphurous acid, showing thus, that a reduction took place and a blue substance was formed. As soon as sulphurous acid ceased to be evolved, heating was stopped.

Part of the blue substance was suspended in the liquid, subsiding after two or three days and then beginning to oxidize to tungstic acid. The clear, colorless, supernatant acid liquid, when treated with water, gave a precipitate of pure, yellow tungsten trioxide. On this account the dark blue substance in the flask was not washed with water but with alcohol and then ether, preventing, as much as possible, contact with the air as long as it was not perfectly dry.

In the subsequent experiments the heating, washing, and drying were made in an atmosphere of carbon dioxide.

The blue substance, once dried, is very stable. It precipitates metallic silver from a solution of silver nitrate and is readily oxidized to tungsten trioxide when ignited. Treated with ammonia, a gray metallic powder is formed which, according to analyses, is metallic tungsten.

0.1265 gram gray substance gave 0.1588 gram tungsten trioxide, equal to 0.1259 gram tungsten, or 99.53 per cent. tungsten.

The ammoniacal liquid, treated with hydrochloric acid, deposited yellow tungstic acid.

Several ignitions of the blue substance to tungsten trioxide, gave an average of 92.08 per cent. tungsten, corresponding well with the requirements of the formula of the monoxide of tungsten, WO, containing theoretically ninety-two per cent. tungsten.

*Experiment 1.*—0.0957 gram blue substance gave 0.1114 gram tungsten trioxide, or 0.0883 gram tungsten, or 92.25 per cent. tungsten.

*Experiment 2.*—0.1923 gram blue substance gave 0.2232 gram tungsten trioxide, or 0.1770 gram tungsten, or 92.03 per cent. tungsten.

*Experiment 3.*—0.2835 gram blue substance gave 0.3292 gram tungsten trioxide, or 0.2611 gram tungsten, or 92.02 per cent. tungsten.

Having determined the percentages of the tungsten, it was thought that a determination of the oxygen would be still more convincing. A weighed quantity of the blue substance was accordingly reduced in a current of hydrogen, the water from the reduction being collected in a weighed U-tube filled with freshly calcined calcium chloride.

*Exberiment 1.*—0.5588 gram blue substance gave 0.0498 gram water, or 0.0437 gram oxygen, or 7.02 per cent. oxygen, thus proving conclusively that the blue substance is the *monoxide of tungsten.*

When we consider the decomposition of the monoxide of tungsten by ammonia into metallic tungsten and a soluble tungstate, we must come to the conclusion that tungsten monoxide, WO, is not formed by the union of only one atom of tungsten and one atom of oxygen, but must be more complicated, perhaps $W_2O.WO_2$, which would correspond to tungstous acid.

The clear, colorless sulphuric acid solution obtained from the treatment of metallic tungsten with concentrated sulphuric acid, upon addition of water, precipitates yellow tungstic acid without passing first through the green and blue stages of oxidation. Evaporated in a platinum dish, it soon takes a dark brown color, almost black, and becomes very viscous; if water is added, a brown flocculent, very rapidly oxidizable precipitate is formed. On trying to filter, it oxidized very rapidly, so that it was impossible to obtain a homogeneous mass.

The color and behavior of this precipitate leads me to the supposition that it is *tungsten dioxide*, which shows the same properties when prepared in the wet way.

If we continue to evaporate to dryness, a brilliant, black, amorphous, very hygroscopic residue is left, which can be quite strongly heated, without any apparent change.

Several attempts were made to prepare a larger quantity of this black substance, but being very light, the greatest part is carried off by the heavy sulphuric acid fumes, very little remaining in the dish, not enough to make an analysis.

To determine the state of oxidation of the tungsten in the sulphuric acid solution, ten cc. of it were added to 190 cc. of standard potassium permanganate. Tungstic acid was precipitated; and titrating with a ferrous salt, almost no change was observed

in the standard of the permanganate, the difference being due only to the dilution. This means that the tungsten is in the sulphuric acid solution in its highest state of oxidation, and that it forms with sulphuric acid, like molybdenum, the anhydride of the sulphotungstic acid

$$WO_3.SO_3 = SO_2<\begin{matrix}O\\O\end{matrix}>WO_2$$

which differs from that of molybdenum by its stability; that of molybdenum soon begins to take on a greenish color, indicating a reduction.

The formation of the sulphotungstic anhydride is also analogous to the combination of uranyl ($UO_2$) with acid radicals, as $UO_2.SO_4$, etc.

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If instead of treating tungsten with concentrated sulphuric acid at a low temperature, it be heated to the boiling-point of the acid, the evolution of sulphurous acid is violent, and two different substances will be seen floating in the liquid, one blue and the other white, settling down when the reaction is completed. These two substances were separated with great difficulty by an operation similar to "panning" with alcohol, then washing with ether and drying in an atmosphere of carbon dioxide.

Tungsten was determined in the greenish-blue substance by ignition and weighing of the resulting tungstic acid.

*Experiment 1.*—0.4796 gram greenish-blue substance gave 0.5688 gram tungsten trioxide, or 0.4511 gram tungsten, or 94.02 per cent. tungsten.

*Experiment 2.*—0.2239 gram greenish-blue substance gave 0.2644 gram tungsten trioxide, or 0.2096 gram tungsten, or 93.61 per cent. tungsten. From this the formula $W_4O_3$ is deduced, containing theoretically 93.87 per cent. tungsten.

In group VI of the elements we do not find another similar oxide, with the exception of that of uranium, $U_4O_3$, prepared by Peligot, by treating a solution of $U_4Cl_3$ with ammonia. It is a light green-colored, rather unstable compound.

The quantity of oxygen in $W_4O_3$ was determined by reducing it in a current of hydrogen, as in a former experiment.

*Experiment.*—0.5321 gram greenish-blue substance gave 0.0358 gram water, or 0.0318 gram water, or 5.97 per cent. oxy-

gen, corresponding to the theoretical requirement of the formula, 6.13 per cent. oxygen.

$W_4O_3$ is decomposed by ammonia into metallic tungsten and tungstic acid; it precipitates silver from a solution of silver nitrate, insoluble in acids. The sulphuric acid solution, from the treatment of metallic tungsten with concentrated sulphuric acid, has the same properties as that obtained at a low temperature.

## III.

### ACTION OF SULPHURIC ACID UPON METALLIC TUNGSTEN IN SEALED TUBES.

Sulphuric acid being so easily reduced by metallic tungsten at the ordinary atmospheric pressure, it was necessary to see what results would be obtained by allowing these two substances to act upon each other in sealed tubes and at different temperatures.

One gram of pure metallic tungsten and forty cc. of concentrated sulphuric acid were heated in a sealed tube for five hours at 105° C. At this temperature almost no reaction took place, so I increased the temperature to 150° C. for seven hours.

The contents of the tube had an entirely different appearance; there was a beautiful, clear, dark blue liquid, and a solid body of the same color, strongly adhering to the sides of the tube. Opening the tube, a very large quantity of sulphurous acid escaped with great violence.

The blue substance was well washed with alcohol and then ether, and dried at 100° C., in an atmosphere of carbon dioxide. It is a homogeneous, dark blue mass, that precipitates metallic silver in brilliant scales, from a solution of silver nitrate; ammonia and alkalies decompose it into metallic tungsten and a soluble tungstate; the metallic tungsten proved to be very pure.

0.2115 gram gray substance gave 0.2667 gram tungsten trioxide, or 0.2115 gram tungsten, or 100 per cent. tungsten.

On adding water to the blue sulphuric acid solution, a green precipitate is formed, which in time becomes yellow from the oxidation to tungstic acid.

The blue substance, when ignited, is immediately transformed into yellow tungsten trioxide, from which the percentage of tungsten was calculated:

*Experiment 1.*—0.2512 gram blue substance gave 0.2802 gram tungsten trioxide, or 0.2221 gram tungsten, or 88.41 per cent. tungsten.

*Experiment 2.*—0.2136 gram blue substance gave 0.2493 gram tungsten trioxide, or 0.1977 gram tungsten, or 88.41 per cent. tungsten.

*Experiment 3.*—0.2555 gram blue substance gave 0.2848 gram tungsten trioxide, or 0.2258 gram tungsten, or 88.38 per cent. tungsten.

These three analyses were made with the product of three different tubes and correspond very well with the requirements of the formula of the tungsten sesquioxide :

$$W_2O_3 = WO.WO_2,$$

containing theoretically 88.46 per cent. tungsten.

The quantity of oxygen was also determined by reduction in a current of hydrogen. The metallic tungsten remaining in the boat also corresponds to the formula of the sesquioxide.

0.4111 gram blue substance gave 0.0530 gram water, or 0.0473 gram oxygen, or 41.52 per cent. oxygen.

0.3577 gram tungsten equals 88.44 per cent. tungsten.

This oxide has a great similarity to the sulphur sesquioxide ($S_2O_3$), which element belongs to the same group of the periodic system as tungsten. The sesquioxide of sulphur is decomposed by water into sulphur, sulphurous acid, and sulphuric anhydride ($SO_3$) and dissolves with a blue color in concentrated sulphuric acid. The difference between tungsten sesquioxide and sulphur sesquioxide is that the former is decomposed by ammonia, instead of by water, into metallic tungsten and tungsten trioxide ; probably tungsten dioxide is also formed but, being very unstable, it oxidizes very rapidly to tungsten trioxide.

The analogy between tungsten and sulphur is further shown by the property of silver sulphite to be decomposed by water into metallic silver and sulphuric acid.

The two equations demonstrate the analogy:

$$Ag_2O.SO_2 + O\begin{matrix}H\\H\end{matrix} = 2Ag + SO_2<\begin{matrix}OH\\OH\end{matrix};$$

$$WO.WO_2 + \begin{matrix}OHNH_4\\OHNH_4\end{matrix} = W + WO_2<\begin{matrix}O(NH_4)\\O(NH_4)\end{matrix} + H_2O,$$

so we can consider $W_2O_3$ to be the tungstite of tungsten.

Molybdenum sesquioxide differs from that of tungsten, by not being decomposed by ammonia or the alkalies. Chromium sesquioxide ($Cr_2O_3$) differs by not being reduced by hydrogen, is not affected by heat, and is insoluble in acids.

To investigate the influence of heat in the reaction of sulphuric acid upon metallic tungsten, in sealed tubes, one gram of metallic tungsten was introduced into several tubes with varying quantities of concentrated sulphuric acid, and heated between 170° and 180° C., for seven hours. The tubes contained a blue liquid and a homogeneous blue substance. Upon opening them, sulphurous acid escaped. The blue substance was washed with alcohol and ether and then dried at 100° C. in an atmosphere of carbon dioxide.

This blue substance is of a lighter shade than the sesquioxide, is soluble in concentrated sulphuric acid, precipitates metallic silver from a solution of silver nitrate, and is decomposed by ammonia into metallic tungsten and tungstic acid.

Addition of water to the blue, sulphuric acid solution will precipitate a greenish-blue body, which becomes yellow ($WO_3$) when it stands for some time. A certain quantity of this blue solution which had stood for three weeks in a small flask not well corked, changed its blue color to dark green, remaining perfectly clear. The sulphurous acid which it contained was driven off by passing a current of carbon dioxide until it was perfectly odorless; five cc. were then added to 190 cc. of standard potassium permanganate so as to find the state of oxidation of the tungsten. The quantity of tungsten was determined by precipitating the tungstic acid in ten cc. of the green solution, by addition of water. From different experiments the writer concluded that the green substance in solution must be $W_5O_{12}$.

Muthmann[1] has obtained the same oxide of molybdenum ($Mo_5O_{12}$), by treating, in a flask, metallic molybdenum with concentrated sulphuric acid, at a low temperature.

This experiment was repeated several times between 170° and 180° C., always obtaining the same blue compound:

*Experiment 1.*—0.3651 gram blue substance gave 0.3992 gram tungsten trioxide, or 0.3166 gram tungsten, or 86.71 per cent. tungsten.

[1] *Loc. cit.*

*Experiment 2.*—0.2644 gram blue substance gave 0.2881 gram tungsten trioxide, or 0.2285 gram tungsten, or 86.43 per cent. tungsten.

*Experiment 3.*—0.3272 gram blue substance gave 0.3575 gram tungsten trioxide, or 0.2835 gram tungsten, or 86.70 per cent. tungsten.

*Experiment 4.*—0.2837 gram blue substance gave 0.3096 gram tungsten trioxide, or 0.2455 gram tungsten, or 86.53 per cent. tungsten.

From these results is deduced the following formula:

$$W_5O_9 = WO_3.2W_2O_3,$$

containing theoretically 86.47 per cent. tungsten.

Oxygen was determined by reducing the blue substance in a current of hydrogen gas, as in former experiments.

0.4561 gram blue substance gave 0.0690 gram water, or 0.0614 gram oxygen, or 13.46 per cent. oxygen, corresponding well to the formula $W_5O_9$ with 13.53 per cent. oxygen.

A third series of experiments in sealed tubes was made at temperatures varying from 200°–250° C.

These results were not satisfactory, no homogeneous compounds, but mixtures of various colors, being obtained.

In tubes heated at 250° C. it was possible to see some yellow tungstic acid and, contrary to all former experiments, the sulphuric acid was perfectly colorless; probably higher oxides were formed, which are insoluble in sulphuric acid, whereas the lower oxides are soluble.

These traces of tungstic acid led to the hope that by increasing the temperature and heating for a long time, the metallic tungsten could be completely oxidized to tungstic acid; but all attempts were fruitless, probably on account of not being able to obtain a temperature sufficiently high.

## IV.

### ACTION OF SULPHUROUS ACID UPON METALLIC TUNGSTEN.

In one of the former experiments, where metallic tungsten was treated with concentrated sulphuric acid in an open flask at the ordinary atmospheric pressure, a few grains of the metal adhered to the neck of the flask far above the sulphuric acid.

When the reaction began by evolving sulphurous acid,

those grains of metallic tungsten slowly changed their color, becoming first green and then blue. As the temperature was low the tungsten could not have been oxidized by the oxygen from the air, as in ignition, and, as the reaction in the flask took place very gently, no sulphuric acid was thrown on the grains, so that the only explanation for this oxidation is that the sulphurous acid was readily reduced by tungsten.

This observation suggested the examination of the action of sulphurous acid upon tungsten under different conditions.

A small quantity of metallic tungsten was spread out in a hard glass tube, so as to offer a large surface for the action of the sulphur dioxide prepared by reducing sulphuric acid with copper. When all the air from the apparatus was driven out I began to heat the tungsten gently, but no reaction took place. Heating stronger to dull red, the gray color of the metal slowly began to become blue. When the whole mass appeared to be homogeneous, heating was discontinued, and the mass allowed to cool in the current of sulphur dioxide. Examining this blue substance carefully under the microscope a brown body seemed to be mixed with it, which was probably tungsten dioxide.

This experiment was repeated at various temperatures and for varying periods of time, but always more or less brown substance was formed. To prevent some parts of the metal being heated more than others, the tube was slowly turned, constantly exposing in this way new parts of the tungsten to the action of heat and of the sulphurous acid.

Obtaining no satisfactory results, the action of sulphurous acid upon metallic tungsten in sealed tubes was tried.

I first prepared a concentrated solution of sulphurous acid. The gas, after passing through three wash-bottles, entered a flask filled with distilled water, imbedded in a mixture of ice and salt; after complete saturation the contents of the flask, of a gelatinous consistency, was poured into a tube sealed at one end, containing metallic tungsten. During the sealing of the open end of the tube the sealed end was kept in the refrigerating mixture, so as not to lose any gas.

After the tube acquired the temperature of the surrounding air it was heated at 110° C. for ten hours. A green body was formed and a large quantity of free sulphur floated in the liquid.

Another tube was heated at 90° C. for the same length of time, when its contents had exactly the same appearance as that of the first tube.

On opening the tubes, the sulphurous acid escaped with great violence. Separation of the green substance from the free sulphur was tried by different mechanical means, amorphous sulphur being insoluble in carbon bisulphide; being unsuccessful in my attempts, I treated the green substance with carbon disulphide in a sealed tube for about half an hour, at 100° C. This operation succeeded very well, all the sulphur being dissolved. The green substance did not change in appearance; it was washed with water, alcohol, and ether, and dried in an atmosphere of carbon dioxide. The tungsten was determined by ignition.

*Experiment 1.*—0.2625 gram green substance gave 0.2649 gram tungsten trioxide, or 0.2100 gram tungsten, or 80.09 per cent. tungsten.

*Experiment 2.*—0.5012 gram green substance gave 0.5065 gram tungsten trioxide, or 0.4017 gram tungsten, or 80.14 per cent. tungsten.

*Experiment 3.*—0.3267 gram green substance gave 0.3305 gram tungsten trioxide, or 0.2621 gram tungsten, or 80.22 per cent. tungsten.

From these results is calculated the following formula:

$$W_5O_{14} = 4WO_3.WO_2,$$

containing theoretically 80.44 per cent. tungsten.

Knowing now that sulphurous acid will oxidize metallic tungsten, it was interesting to examine how far it would reduce tungstic acid.

The sealed tubes were prepared in exactly the same way as in the former experiments, taking tungstic acid instead of metallic tungsten. At 100° and 125° C. no change took place. At 150° C. the tungsten trioxide began to take a green color and free sulphur was liberated. The liquid was colorless and clear. I repeated this experiment at different temperatures, but did not succeed in obtaining a homogeneous compound.

Two of these tubes were lying on my desk for several months, exposed to the light and the direct rays of the sun. It was observed that the green substance darkened until it had a very dark green color, which apparently did not change any more and was homo-

geneous. One end of the tube was opened, sulphurous acid escaped, and the green substance was rapidly washed with water, but it changed its dark green color to light green again. The free sulphur was separated by dissolving it in carbon disulphide, in a sealed tube; the result was a still lighter green substance, not homogeneous.

These experiments show that tungstic acid is reduced by sulphurous acid, but the resulting lower oxides are not stable. The action of light in this case is very interesting and might be the starting point of some important investigations.

The second tube was kept sealed over one year longer. During this time the dark green color of the substance gradually changed to light green, and on opening the tube no trace of sulphurous acid was perceptible, but instead a very strong odor of hydrogen sulphide. The liquid had a yellow color.

## V.

### ACTION OF HEAT UPON AMMONIUM METATUNGSTATE.

$$W_4O_{13}(NH_4)_2 + 8H_2O.$$

Berlin,[1] obtained an oxide of molybdenum, which, according to his analyses, has the formula $Mo_3O_8 = 2MoO_3.MoO_2$, a molybdate of molybdenum. He prepared it by heating strongly over a blast lamp, in a platinum crucible, a mixture of two parts of molybdenum trioxide and one part of ammonium molybdate. After cooling, the sides of the crucible were found to be covered with beautiful purple crystals, soluble in ammonia.

Later Muthmann[2] found that this oxide contained a considerable amount of nitrogen, which naturally lowered the percentage of molybdenum in it. He freed it of nitrogen by repeated boiling with hydrochloric acid and determined its formula to be

$$Mo_5O_{13} = 2MoO_3.3MoO_2.$$

On account of the great analogy between tungsten and molybdenum, the same experiment was tried with ammonium metatungstate (one part) and tungstic acid (two parts), heated strongly for one hour over the blast lamp in a covered platinum crucible. The result was a mixture of blue and green oxides and undecomposed tungsten trioxide.

[1] *J. prakt. Chem.*, 49, 447.
[2] *Loc. cit.*

This mode of operating is very unsatisfactory, it being impossible to keep the air away from the contents of the crucible. The same mixture was introduced into a well-covered porcelain crucible and then into a large Battersea crucible, completely imbedded in powdered charcoal, the whole closed with refractory clay; in this way no air could possibly reach the hot contents of the crucible. It was heated for ten hours to white heat, in a wind furnace, and allowed to cool slowly over night. Opening the small crucible the sides were found covered with a beautiful crystalline substance of all possible colors.

Evidently, a reduction took place, but probably an inadequate quantity of the reducing agent was present to complete the reduction. As in this case, the hydrogen of ammonium metatungstate is the reducing agent, the experiment was repeated, taking the metatungstate alone and heating it for ten hours to a white heat.

The porcelain lid was fused to the crucible so that it had to be broken to reach its contents, which consisted of a perfectly homogeneous, gray, crystalline metallic substance, with a yellow reflex like brass filings, according to the exposure to the light. These crystals were carefully collected, a weighed quantity ignited and, from the tungstic acid obtained, it was concluded that it was metallic tungsten.

*Experiment 1.*—0.2429 gram gray crystals gave 0.3068 gram tungsten trioxide, or 0.2426 gram tungsten, or 99.87 per cent. tungsten.

*Experiment 2.*—0.1138 gram gray crystals gave 0.1434 gram tungsten trioxide, or 0.1137 gram tungsten, or 99.91 per cent. tungsten.

The temperature has a great influence in all these experiments upon the final result. Another experiment was performed by heating ammonium metatungstate for one and a half hours, only to bright red instead of to a white heat. The crucibles were prepared as in the foregoing experiments.

The small crucible, after the operation, contained a beautiful purple substance, with a yellow metallic reflex, insoluble in water, acids, and alkalies. It precipitated metallic silver from an ammoniacal solution of silver nitrate and easily burned to tungsten trioxide.

*Experiment 1.*—0.4075 gram purple substance gave 0.4181 gram tungsten trioxide, or 0.3315 gram tungsten, or 81.35 per cent. tungsten.

*Experiment 2.*—0.3112 gram purple substance gave 0.3183 gram tungsten trioxide, or 0.2524 gram tungsten, or 81.09 per cent. tungsten.

*Experiment 3.*—0.3626 gram purple substance gave 0.3713 gram tungsten trioxide, or 0.2945 gram tungsten, or 81.21 per cent. tungsten.

*Experiment 4.*—0.3874 gram purple substance gave 0.0819 gram water, or 0.0727 gram oxygen, or 18.78 per cent. oxygen.

0.3146 gram tungsten, or 81.20 per cent. tungsten.

From this was calculated the formula,

$$W_3O_8 = 2WO_3.WO_2,$$

which would be the tungstate of the tungsten dioxide containing theoretically 81.17 per cent. tungsten and 18.83 per cent. oxygen.

In Roscoe and Schorlemmer's treatise, Vol. 2, p. 208, mention is made of a blue oxide, to which the formula $W_3O_8$ is given. It was obtained by reducing tungstic acid in a current of hydrogen at 250° C. No properties of the oxide are given.

As small quantities of nitrogen could be occluded by the purple substance or even chemically combined, a small quantity of it was ignited in a current of hydrogen and the escaping gas conducted into a dilute cochineal solution. After one hour of this treatment the reduction was complete, but the cochineal solution had not changed in the least, demonstrating the complete absence of nitrogen.

Cochineal is a very delicate test for ammonia, the least trace changing its color to purple.

The substance remaining in the boat corresponds well with the requirements of the formula $W_3O_8$ (81.17 per cent. tungsten).

0.3462 gram purple substance gave 0.2813 gram tungsten, or 81.25 per cent. tungsten.

## VI.

### ACTION OF ETHYLENE UPON TUNGSTIC ACID.

The well known property of ethylene of decomposing by heat into acetylene and methane, which in turn is decomposed

into acetylene and hydrogen, afforded a new method of reducing tungstic acid by nascent hydrogen, and not by the wet way, which necessarily must lead to new results.

A small quantity of tungsten trioxide was spread out in a hard glass tube and a rapid current of ethylene ($C_2H_4$) passed through to expel all the air from the apparatus.

The ethylene gas was prepared by introducing drop by drop from a separating funnel a mixture of one part of alcohol and two parts of sulphuric acid into a flask containing twenty-five grams of absolute alcohol and 550 grams of sulphuric acid, heating very gently on a sand-bath. Ethylene gas prepared in this way always contains sulphurous acid and carbon dioxide; to free it from these admixtures it was conducted through three wash-bottles containing a concentrated solution of caustic potash, then through two towers, one filled with pieces of caustic potash, the other with calcined calcium chloride. The gas thus purified and dried, entered the tube containing the strongly heated tungstic acid. From time to time, the tube was turned, so as to offer fresh surfaces to the action of the heat and ethylene gas.

Soon the yellow color of the trioxide began to change and in a short time the whole quantity was transformed into a dark blue, homogeneous substance, retaining the crystalline form of the trioxide used. In the cold part of the tube minute drops of water were condensed.

After cooling in the current of ethylene, a weighed quantity of the blue substance was ignited in an open porcelain crucible. It oxidized very rapidly to yellow tungstic acid, but great was my astonishment, when weighing, to find that the weight of the tungstic acid *did not differ from that of the blue substance before the ignition*.

*Experiment 1.*—0.4037 gram blue substance gave 0.4037 gram tungsten trioxide.

*Experiment 2.*—0.4462 gram blue substance gave 0.4461 gram tungsten trioxide.

*Experiment 3.*—0.1152 gram blue substance gave 0.1150 gram tungsten trioxide.

*Experiment 4.*—0.1150 gram blue substance gave 0.1150 gram tungsten trioxide.

The presence of carbon being possible in this substance, a

combustion was made as with an organic substance. After heating strongly for five hours, the U-tube and potash bulbs were weighed, but there was no appreciable change of weight, showing complete absence of carbon and hydrogen.

Only in two ways can the writer explain this phenomenon. Either the substance is a new modification of tungstic acid, which is not probable on account of the formation of traces of water when treating tungstic acid with ethylene, or it is an oxide coming very near the limit of tungstic acid, and its molecular weight being so high that the small increase of weight when igniting it to tungstic acid cannot be determined.

The blue substance is insoluble in acids and alkalies, and does not precipitate silver from a solution of silver nitrate.

The action of acetylene ($C_2H_2$) upon tungstic acid at different temperature was also tried, but in no case could any change be found in the appearance of the trioxide.

Only a very small deposit of carbon could be seen, due to the decomposition of acetylene by the heat.

## VII.

### ACTION OF THE OXIDES OF CARBON UPON TUNGSTIC ACID.

Muthmann[1] studied the action of carbon monoxide upon molybdic acid and succeeded in reducing it to metallic molybdenum.

The same reduction was tried with the tungstic acid, heating it strongly in a current of carbon monoxide, prepared by treating oxalic acid with sulphuric acid, conducting the escaping gas through two wash-bottles containing a strong solution of caustic potash, to retain any carbon dioxide, and then through two towers filled with calcium chloride. After five hours of intense heating in the boat, three distinct, differently colored layers were found; at the bottom the substance was brown, the second layer was blue, and the top layer was almost unaffected tungstic acid. The same portion was heated for five hours more, the brown substance increasing in quantity. It was then heated for over twenty hours, but no homogeneous substance could be obtained.

This shows the great affinity of tungsten for oxygen. Muthmann obtained metallic molybdenum after ten hours of the same

[1] *Loc. cit.*

treatment, whereas tungsten after thirty hours was still in the form of oxides.

When $U_3O_8$ is heated for a long time in a current of carbon dioxide it is decomposed to $U_2O_3$.

Tungsten trioxide was subjected to the same treatment, heating a weighed quantity in a platinum crucible and introducing into it a current of dry carbon dioxide. Two hours of heating over the blast-lamp produced no change.

## VIII.

### ACTION OF ALKALI METALS AND HALOID SALTS UPON TUNGSTIC ACID.

*A. Action of Potassium Bromide.*—It was found that if tungstic acid is heated with a solution of potassium bromide and a few drops of hydrochloric acid, a reaction takes place. The solution takes on a green color which, upon continued heating, again becomes yellow. This reduction led to the idea that by fusing a mixture of potassium bromide and tungstic acid, well-defined bodies could be obtained.

Three grams of tungstic acid and ten grams of potassium bromide, thoroughly mixed, were introduced into a well-covered porcelain crucible and then imbedded in powdered charcoal in a larger crucible, as in former experiments, and the whole heated to white heat for six hours in a wind furnace. After thorough cooling the small crucible was opened and a gray, crystalline metallic powder was found. After washing it with water and drying at 110° C., a weighed quantity was ignited; it burned rapidly to yellow tungstic acid.

*Experiment 1.*—0.0987 gram gray substance gave 0.1238 gram tungsten trioxide, or 0.0982 gram tungsten, or 99.5 per cent. tungsten.

*Experiment 2.*—0.3384 gram gray substance, gave 0.4266 gram tungsten trioxide, or 0.3383 gram tungsten, or 99.97 per cent. tungsten.

This gray substance is consequently metallic tungsten.

The same mixture was treated at different temperatures and for varying periods, but no well-defined bodies were obtained; probably by varying the proportions of the two substances, other well-defined compounds would result.

*B. Action of Potassium Iodide.*—Schulze[1] fused potassium iodide and tungstic acid, but does not seem to have obtained any well-defined bodies, as he does not give any analytical results.

Two grams of potassium iodide and one gram of tungstic acid were treated as in the experiments under *A*.

The small crucible contained a beautiful purple, crystalline substance, precipitating metallic silver from an ammoniacal solution of silver nitrate, insoluble in acids and alkalies. This substance has all the characteristics of that obtained from the action of heat upon metatungstate of ammonium. The amount of tungsten calculated from the tungstic acid obtained by ignition of a weighed quantity of the purple substance, corresponds well with the requirements of the formula $W_3O_8$, with 81.17 per cent. tungsten.

*Experiment 1.*—0.2131 gram purple substance gave 0.2181 gram tungsten trioxide, or 0.1729 gram tungsten, or 81.14 per cent. tungsten.

*Experiment 2.*—0.3127 gram purple substance gave 0.3202 gram tungsten trioxide, or 0.2539 gram tungsten, or 81.19 per cent. tungsten.

Another mixture of one gram tungstic acid and four grams potassium iodide, after the same treatment as above, gave quite a different result. Metallic tungsten was obtained.

0.1225 gram gray powder gave 0.1544 gram tungsten trioxide, or 0.1224 gram tungsten, or 99.98 per cent. tungsten.

*C. Action of Potassium Chloride.*—One gram tungstic acid and two grams potassium chloride, were treated as under *B*, for five hours. The sides of the crucible were covered with beautiful, glittering, gray crystals, which were metallic tungsten.

0.1066 gram gray powder gave 0.1340 gram tungsten trioxide, or 0.1065 gram tungsten, or 99.90 per cent. tungsten.

The action of the haloid salts of the other alkali metals was also studied, and it was found that the reducing power diminishes with the lower atomic weight; the temperature must be higher and the action of heat longer.

*D. Action of Metallic Potassium.*—The remarkable reducing action of the haloid salts of the alkali metals cannot be explained otherwise than that at a very high temperature they are dissocia-

[1] *J. prakt. Chem.*, 21, 439.

ted into their component parts. The alkali metal being, so to say, in the nascent state, combines with eagerness with the oxygen of the tungstic acid and sets free metallic tungsten.

The bottom of a porcelain boat was covered with small, bright pieces of metallic potassium, and on top of it tungstic acid. The whole was introduced into a hard, glass tube, through which a current of dry nitrogen passed; the nitrogen was prepared by dropping a concentrated solution of sodium nitrite into a hot, concentrated solution of ammonium chloride, the gas passing through two calcium chloride towers, before entering the tube. After all the air was expelled from the apparatus, the tube was gently heated under the boat, increasing the temperature slowly, until the potassium began to melt. Soon white vapors began to rise from the boat, condensing to a white powder in the cooler parts of the tube. Increasing the temperature a little, blue and purple fumes of the different oxides of potassium were formed. The reduction began to be violent, when suddenly a deflagration took place, and all action ceased immediately.

The boat was allowed to cool in the atmosphere of nitrogen. It contained a gray, spongy mass, fused to the side of the boat and covered with a white coating ($K_2O$). After washing with water, a gray metallic, very finely divided powder was left, which was metallic tungsten.

0.1892 gram gray powder gave 0.2385 gram tungsten trioxide, or 0.1891 gram tungsten, or 99.91 per cent. tungsten.

If, instead of washing the contents of the boat with water, hydrochloric acid is used, a clear, dark blue solution is obtained, which oxidizes very rapidly to a green-colored liquid and then a yellow-greenish precipitate is formed, which in time becomes entirely yellow. The supernatant liquid is colorless and clear. The undissolved residue in the boat is gray metallic tungsten.

0.1965 gram gray powder gave 0.2477 gram tungsten trioxide, or 0.1964 gram tungsten, or 99.95 per cent. tungsten.

*E. Action of Metallic Sodium*—The previous experiment was repeated, but instead of potassium, metallic sodium was used.

The reaction takes place at a higher temperature, is not so violent, and the deflagration liberates less heat. The contents of the boat were much darker in color after being washed. The substance is almost black and flocculent, burning rapidly to

tungstic acid when ignited. It proved to be metallic tungsten.

0.1190 gram black substance gave 0.1500 gram tungsten trioxide, or 0.1189 gram tungsten, or 99.91 per cent. tungsten.

## IX.

### ACTION OF METALLIC MAGNESIUM UPON TUNGSTIC ACID.

As magnesium is a much less active element than the alkali metals, the writer thought that perhaps it would enable him to obtain new oxides.

In a porcelain boat was placed a mixture of one gram tungstic acid and 0.75 gram metallic magnesium powder, the whole introduced into a hard glass tube and a current of dry nitrogen passed over it. The tube was gently heated under the boat until it was dull red in color, when a violent deflagration took place, generating so much heat that the tube became quite red, and broke in several places.

After cooling in the atmosphere of nitrogen the boat was taken out; it contained a very hard, gray substance, firmly adhering to the sides of the boat. It was covered with magnesium oxide and emitted a peculiar, garlic-like odor. After detaching this gray mass from the sides of the boat, it was ground in a mortar to a fine powder. On adding a little water, it began to effervesce strongly. The escaping gas was collected in a test-tube, and in bringing it to a flame, a little puff was heard, showing the decomposition of water.

Neither magnesium nor tungsten decompose water at the ordinary temperature. Then this powder must be an alloy of the two metals.

A certain quantity of the gray substance was left on the sides of the boat, to which was added a drop of hydrochloric acid; a little explosion occurred, with a blue flame. This explosion is due to a magnesium silicide, formed by heating magnesium strongly in contact with the silicon of the porcelain boat,

$$Si_2Mg_5 = Mg_3Si_2 + SiMg_2,$$

which is easily decomposed by hydrochloric acid, the free silicon forming with hydrogen, siliconhydride, $SiH_4$, an inflammable gas at the ordinary temperature.

This experiment of the reduction of the tungstic acid with magnesium in an *iron* boat was repeated, to prevent the formation of the

magnesium silicide. The result was a gray mass as before, decomposing water and generating hydrogen when treated with hydrochloric acid; the residue is then insoluble in acids, except in aqua regia, and is an alloy of magnesium and tungsten.

Filtering off the hydrochloric acid from the gray mass, the drops toward the end of the funnel were seen to take on a dark blue color, which during the fall to the bottom of the flask changed to yellow without forming any precipitate. If water is added to this filtrate yellow tungstic acid is precipitated.

A portion of the gray mass was treated with hydrochloric acid in an atmosphere of carbon dioxide, filtered in the same gas into a flask also filled with it. In this case the hydrochloric acid solution did not take first a blue color, but it immediately became yellow, and water did not precipitate tungstic acid in the cold, but only upon heating.

To determine the state of oxidation of the tungsten in this solution, ten cc. were added to 190 cc. of potassium bichromate solution (tenth-normal), but its standard did not change, showing that the tungsten is at its highest state of oxidation and must form like molybdenum, an oxychloride of tungsten,

$$WO_3.2HCl.$$

This oxychloride of tungsten is probably analogous to chlorochromic acid, $CrO_2 < \begin{matrix} Cl \\ OH \end{matrix} = CrO_3.HCl$, and to chlorosulphonic acid, $SO_2 < \begin{matrix} Cl \\ OH \end{matrix} = SO_3.HCl$, being decomposed when heated into anhydride.

The gray substance precipitates metallic silver from a solution of silver nitrate. As it dissolves with difficulty even in aqua regia, I fused it with potassium bisulphate, obtaining soluble magnesium sulphate and insoluble tungstic acid, which were separated by filtration. In the filtrate magnesium was precipitated as magnesium-ammonium phosphate.

0.4598 gram gray substance gave 0.4179 gram tungsten trioxide, or 0.3314 gram tungsten, or 72.08 per cent. tungsten.

0.5916 gram gave 0.1279 gram magnesium pyrophosphate or 27.81 per cent. magnesium.

Different experiments gave about the same results, with slight variations.

Instead of reducing the tungstic acid with magnesium in a current of nitrogen, carbon dioxide was used. The reduction took place very slowly, at a very high temperature, and without deflagration. The resulting product had the color of steel, decomposed in water, and apparently also absolute alcohol when hot.

## THE OXYNITRIDES OF TUNGSTEN.

### I.

#### ACTION OF AMMONIUM CHLORIDE UPON TUNGSTIC ACID.

Continuing the experiments of the reduction of tungstic acid by various reducing agents, a large number of bodies containing tungsten, nitrogen, and oxygen were the result.

No suboxides or true nitrides of tungsten could be obtained, the affinity of tungsten to oxygen being so great that it was impossible to substitute the last traces of oxygen by nitrogen.

A long series of experiments was made under varying conditions, and the conclusion was drawn that nitrides of tungsten can be obtained only by treating the chlorides of tungsten.

Ammonium chloride being easily dissociated by heat, a mixture was made of tungstic acid and ammonium chloride in excess and heated in a covered porcelain crucible over the blast lamp, until no more fumes were evolved. Opening the crucible, there was found on the top some slightly decomposed tungstic acid, underneath a mixture of blue and green oxides, and at the bottom a black crystalline substance. Some of the crystals reflected the light so strongly that they were first taken to be some small pieces of glass that had accidentally found their way into one of the reagents used.

This black substance was again twice treated with ammonium chloride, succeeding in this way in obtaining a homogeneous, black, very light substance, insoluble in acids and alkalies.

The sides of the crucible were covered with a black, metallic deposit, which suggested the presence of nitrogen on account of its similarity with nitrides of chromium and uranium.

To ascertain the presence or absence of nitrogen, the well washed and dried black substance was treated in a hard glass tube with hydrogen, the gas escaping from the tube being conducted into a cochineal solution, which changed its color very

soon to purple, thus showing the formation of ammonia, and consequently the presence of nitrogen in the black substance. A nitride was obtained instead of a lower oxide. The nitrogen was estimated by Dumas' method.

It was also important to know whether this substance contained hydrogen. A weighed quantity was ignited in a current of oxygen, taking all precautions to prevent the formation of nitrogen oxides. Any water formed was absorbed in a U-tube, filled with freshly calcined calcium chloride. After five hours heating, the increase of weight of the U-tube was only 0.0002 gram, corresponding to 0.08 per cent. hydrogen, so that hydrogen is absent.

If the black substance is ignited in a current of hydrogen abundant water vapors are condensed in the cooler parts of the tube, showing the presence of oxygen.

The tungsten was estimated by igniting a weighed quantity of the black substance in an open crucible. Even prolonged and very strong heating will not oxidize it completely to yellow tungstic acid. In one experiment the substance was ignited for two days, taking every precaution to prevent the combustion gases from the burner entering the crucible; but pure yellow tungsten trioxide was not obtainable, a large quantity remaining black, some being dark and some light green. To complete the oxidation I had to use aqua regia repeatedly and obtained in this way an almost complete oxidation; the tungstic acid still had a greenish tint.

All the oxynitrides, obtained by different methods, are oxidized with difficulty, showing a great affinity between tungsten and nitrogen; even aqua regia breaks down this intimate union of the two elements only after long action.

*Experiment 1.*—0.2837 gram black substance gave 0.3188 gram tungsten trioxide, or 0.2528 gram tungsten, or 89.10 per cent. tungsten.

0.2047 gram black substance gave 0.0192 gram nitrogen, or 9.41 per cent. nitrogen.

0.4518 gram black substance gave 0.0077 gram water, or 0.0068 gram oxygen, or 1.51 per cent. oxygen.

From this is deduced the formula $W_{20}N_{27}O_4$.

| | Calculated. | Found. |
|---|---|---|
| Tungsten | 89.28 | 89.10 |
| Nitrogen | 9.16 | 9.41 |
| Oxygen | 1.55 | 1.51 |

*Experiment 2.*—0.1293 gram black substance gave 0.1366 gram tungsten trioxide, or 0.1083 gram tungsten, or 83.75 per cent. tungsten.

0.2718 gram black substance gave 0.03493 gram nitrogen, or 12.85 per cent. nitrogen.

0.5006 gram black substance gave 0.0182 gram water, or 0.0162 gram oxygen, or 3.23 per cent. oxygen.

From this the following formula is derived: $W_2N_4O$.

| | Calculated. | Found. |
|---|---|---|
| Tungsten | 83.63 | 83.75 |
| Nitrogen | 12.72 | 12.85 |
| Oxygen | 3.63 | 3.23 |

*Experiment 3.*—0.3247 gram black substance gave 0.3539 gram tungsten trioxide, or 0.2806 gram tungsten, or 86.44 per cent. tungsten.

0.3192 gram black substance gave 0.02432 gram nitrogen, or 7.61 per cent. nitrogen.

0.4758 gram black substance gave 0.0311 gram water, or 0.0276 gram oxygen, or 5.80 per cent. oxygen.

From this the following formula is calculated: $W_5N_6O_4$.

| | Calculated. | Found. |
|---|---|---|
| Tungsten | 86.14 | 86.44 |
| Nitrogen | 7.86 | 7.61 |
| Oxygen | 5.99 | 5.81 |

*Experiment 4.*—0.1997 gram black substance gave 0.2213 gram tungsten trioxide, or 0.1755 gram tungsten, or 87.88 per cent. tungsten.

0.3125 gram black substance gave 0.02176 gram nitrogen, or 6.96 per cent. nitrogen.

0.3894 gram black substance gave 0.0222 gram water, or 0.0198 gram oxygen, or 5.08 per cent. oxygen.

From this the following formula is derived: $W_3N_3O_2$.

| | Calculated. | Found. |
|---|---|---|
| Tungsten | 88.17 | 87.88 |
| Nitrogen | 6.71 | 6.96 |
| Oxygen | 5.11 | 5.08 |

Hoping to obtain better results by increasing the temperature, a mixture of ten grams tungstic acid and twenty grams of ammonium chloride was made in a well-covered, smooth crucible, the whole placed in a large crucible, then filled with powdered charcoal and closed with a lid and fire-clay, so that no air could possibly affect the reduction. It was heated in a wind furnace to bright redness for five hours. After thorough cooling, the small crucible was opened and several crystalline substances of different colors were found.

Different proportions of the mixture and different temperatures were tried, but a homogeneous substance could not be obtained. Finally a mixture was made of ten grams of tungstic acid and sixty grams ammonium chloride, heated to white heat for twelve hours and a black, amorphous powder obtained, insoluble in acids and alkalies, and attacked with difficulty by aqua regia.

0.3278 gram black powder gave 0.4099 gram tungsten trioxide, or 0.3250 gram tungsten, or 99.14 per cent. tungsten.

Consequently it is metallic tungsten. As it must contain some impurity, probably nitrogen, it was boiled for several hours with hydrochloric acid, frequently changing the acid; after washing it with water and drying at 105° C., a weighed quantity was ignited; the hydrochloric acid had removed most of the impurities.

0.2867 gram black powder gave 0.3609 gram tungsten trioxide, or 0.2863 gram tungsten, or 99.85 per cent. tungsten.

After a great many experiments I came to the conclusion that it is impossible to obtain a nitride by means of ammonium chloride, and that it is also impossible to obtain at will and every time the same well-defined body, the result depending entirely upon the temperature, which cannot be regulated nor controlled in this case.

## II.

### ACTION OF POTASSIUM CYANIDE UPON TUNGSTIC ACID.

If tungstic acid is added to potassium cyanide in fusion it will be completely dissolved without changing the color of the fused cyanide. If we continue the addition of tungstic acid a point will be reached when it will no more be dissolved, but instead a black mass will be formed.

Tungsten trioxide will also be dissolved in an aqueous solution of potassium cyanide. If alcohol is added to this solution, and then ether, a heavy yellow, sometimes brown liquid will separate, which after a few weeks will deposit a black substance insoluble in acids or alkalies.

The black substance obtained by fusing tungstic acid and potassium cyanide, was well washed with water, a difficult operation. Being very light, it takes considerable time to settle, and even the densest filter paper will not retain it.

A qualitative test for nitrogen and oxygen proved the presence of both elements. As potassium cyanide contains carbon, the possibility of its presence in the black substance suggested itself; a combustion, as for organic compounds, showed complete absence of carbon.

A weighed quantity was ignited in an open porcelain crucible, for several hours, adding from time to time a few drops of aqua regia, but it was not possible to obtain a pure yellow tungstic acid, as it persistently retained a greenish color.

Nitrogen was determined as before according to Dumas' method.

0.3744 gram black substance gave 0.3913 gram tungsten trioxide, or 0.3103 gram tungsten, or 82.87 per cent. tungsten.

0.2040 gram black substance gave 0.02027 gram nitrogen, or 9.03 per cent. nitrogen.

0.4001 gram black substance gave 0.0324 gram water, or 0.0288 gram oxygen, or 7.21 per cent. oxygen.

From this the following formula is derived : $W_8N_8O_5$.

| | Calculated. | Found. |
|---|---|---|
| Tungsten | 82.82 | 82.86 |
| Nitrogen | 10.07 | 9.93 |
| Oxygen | 7.19 | 7.21 |

An interesting point remained to be determined : whether the reducing power of the potassium cyanide would increase with the temperature.

To this end a crucible containing ten grams of tungstic acid and fifteen grams potassium cyanide was imbedded in charcoal inside of a large crucible, as in former experiments, and heated to white heat for twelve hours, in a wind furnace. After thorough cooling the small crucible was twisted out of shape, showing that the temperature must have been very high; its

sides were incrusted with small, perfectly round, *bright, silver-white metallic globules*, very brittle, insoluble in acids, and attacked with difficulty even by aqua regia. An ignition showed that these globules were very pure metallic tungsten.

0.1752 gram crushed globules gave 0.2209 gram tungsten trioxide, or 0.1752 gram tungsten, or 99.97 per cent. tungsten.

In the literature of tungsten no mention is found of its preparation in this form.

The same mixture of ten grams tungsten trioxide and fifteen grams potassium cyanide was similarly treated as before, but instead of heating to white heat, it was heated to bright red. The result was a black oxynitride.

0.2431 gram black substance gave 0.2612 gram tungsten trioxide, or 0.2071 gram tungsten, or 85.21 per cent. tungsten.

0.3081 gram black substance gave 0.02295 gram nitrogen, or 7.45 per cent. nitrogen.

0.3724 gram black substance gave 0.0307 gram water, or 0.0272 gram oxygen, or 7.32 per cent. oxygen.

The following formula is derived : $W_7N_8O_7$.

| | Calculated. | Found. |
|---|---|---|
| Tungsten | 85.18 | 85.21 |
| Nitrogen | 7.40 | 7.45 |
| Oxygen | 7.40 | 7.32 |

A thorough mixture of ten grams tungstic acid, ten grams potassium cyanide, and ten grams finely powdered charcoal was treated under the same conditions as before, heating to bright red. A black powder was the result, mixed with the charcoal, which could not be separated, both substances having about the same density.

## III.

### ACTION OF CYANOGEN UPON TUNGSTIC ACID.

As potassium cyanide reduces tungstic acid to metallic tungsten at a very high temperature, it was thought that cyanogen would have perhaps a greater reducing power, and that metallic tungsten could be obtained at a lower temperature.

A porcelain boat containing tungsten trioxide was introduced into a hard glass tube ; after driving out the air from the apparatus with dry cyanogen, prepared by dropping a concentrated solution of potassium cyanide into a hot concentrated solution of copper sulphate, the boat was gently heated. At a red heat

the trioxide began to change its color to brown, which soon became darker, and with the increase of temperature finally black. It is a very beautiful, glossy substance, like velvet, with a bluish tint. Like all the other oxynitrides it is oxidized with difficulty by ignition and aqua regia.

1.1140 gram black substance gave 1.1323 gram tungsten trioxide, or 0.0898 gram tungsten, or 80.61 per cent. tungsten.

0.3814 gram black substance gave 0.1473 gram nitrogen, or 3.86 per cent. nitrogen.

0.3227 gram black substance gave 0.0564 gram water, or 0.0502 gram oxygen, or 15.55 per cent. oxygen.

The following formula is derived: $W_6N_3O_{11}$.

| | Calculated. | Found. |
|---|---|---|
| Tungsten | 80.84 | 80.61 |
| Nitrogen | 3.69 | 3.86 |
| Oxygen | 15.46 | 15.55 |

This experiment was repeated several times, heating as long as twenty hours. The hard glass tube became soft, but no metallic tungsten could be obtained. The result was always an oxynitride.

### SEPARATION OF MOLYBDENUM FROM TUNGSTEN.

When these two metals are together in the form of their trioxides they can be quantitatively separated by Debray's method.[1]

If molybdenum and tungsten are in solution they can be separated by Rose's method. To their solution tartaric acid is added and then a current of hydrogen sulphide is passed in, precipitating the molybdenum as sulphide ($MoS_3$), while tungsten remains in solution.

Friedheim and Meyer[2] found that this method is not quite satisfactory, a certain quantity of molybdenum always escaping the action of the hydrogen sulphide and thus remaining in solution.

Tungstic acid is found to be entirely insoluble in concentrated or dilute sulphuric acid, hot or cold, whereas molybdenum trioxide is very easily and rapidly dissolved, so that we have in this deportment a very simple and exact method for the separation of the two elements.

UNIVERSITY OF PENNSYLVANIA.

1 *Loc. cit.*

2 *Ztschr. anorg. Chem.*, 1, 76.

# THE DISTRIBUTION OF THE PRECIOUS METALS AND IMPURITIES IN COPPER AND SUGGESTIONS FOR A RATIONAL MODE OF SAMPLING.

By Edward Keller.

Received January 8, 1897.

IN order to be able to conduct intelligently the sampling of copper, of various forms and grades, solid or in molten furnace charges, knowledge of this subject is essential. Yet figures and tests have been persistently withheld from publication, and the books at our command give us little or no information. This gap in our literature has led to a series of experiments, the results of which here follow:

Nearly all gold- and silver-bearing copper, destined for shipment, is cast into the form of bars or pigs. For the sampler the question arises: Does copper so cast remain homogeneous, or does it not? If so, no difficulty would occur; but experience teaches us that the cast metal is not homogeneous and this leads to the study of the behavior of the precious metals and impurities in copper, when the latter changes from the molten to the solid state.

For the purpose of the experiments, all available grades of copper were selected, and all of them subjected to the same conditions, which is important for the purpose of proper comparison.

The molten copper, directly obtained from reverberatory and blast furnaces, was cast in a cast iron mold, the sides and bottom of which were one inch thick, and would, therefore, give the copper a fair length of time to chill. The inside dimensions of the mold were: length, ten inches; width, nine inches; and depth five inches, which dimensions were the same for the blocks of copper obtained.

The accompanying figure (1) illustrates the method employed to obtain samples from these blocks. *A* was cut away, and the face thus produced on *B* was marked off over one-half of its surface into one inch squares (it being assumed that the other half would behave the same, or nearly so), and by drilling through the center of each square, three inches deep, the individual samples, as indicated by $S_1$, $S_2$, $S_3$, $S_4$, $S_5$, etc., obtained.

In this way each block should have yielded twenty-five samples. But with the unrefined copper, the uppermost inch of the

block consisted mostly of blisters and some slag, while with the refined material the surface, on setting, had sunken nearly one inch. With all but one block, therefore, twenty samples of each only were considered.

In Fig. 2 are given the silver and gold determinations of a

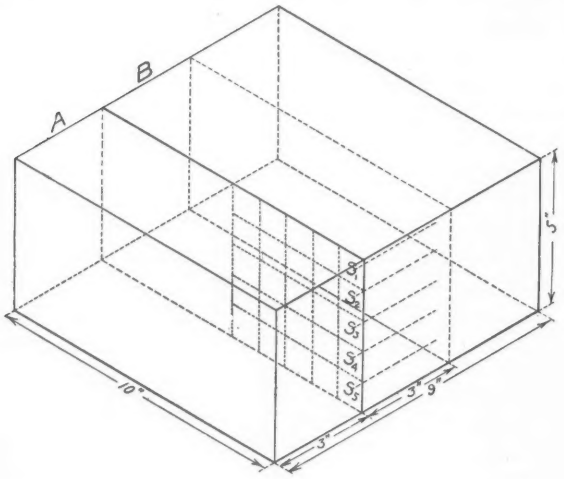


Fig. 1.

blister-copper for the twenty regular samples, as also of the uppermost crust, over the blisters. The amount of the precious

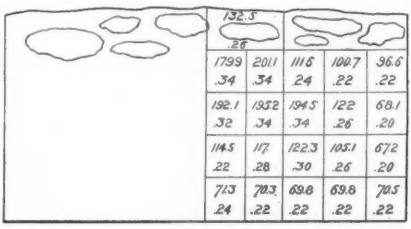


Fig. 2.

metals is expressed in ounces per ton, in this, as well as all the following samples.

For the purpose of a general analysis of this block, samples were taken from the bottom, center, and top of *B* (Fig. 1). They gave the following results:

| | Bottom. Per cent. | Center. Per cent. | Top. Per cent. |
|---|---|---|---|
| Ag | 0.248 | 0.641 | 0.454 |
| Au | 0.00068 | 0.00109 | 0.00089 |
| Pb | 0.002 | 0.058 | 0.019 |
| Bi | 0.005 | 0.055 | 0.024 |
| Sb | 0.048 | 0.157 | 0.099 |
| As | 0.034 | 0.108 | 0.074 |
| Te | 0.004 | 0.027 | 0.019 |
| S | 0.040 | 0.112 | 0.047 |
| | 0.382 | 1.159 | 0.737 |

A glance at these figures convinces us that in this case a concentration, or segregation, of precious metals and impurities has taken place in a high degree towards the center; not the geometrical center but the center of solidification, which latter naturally lies above the former, more heat being given off at the bottom to the metallic mold than to the air on top, for which reason solidification proceeds more rapidly from the bottom.

Of the degree of concentration we best receive an idea by comparing each element of the bottom sample with the corresponding element of the center sample. Dividing the value for the latter by the value for the former, gives us the degree of concentration from bottom to center. We have accordingly:

| Element. | Concentration. |
|---|---|
| Ag | 2.59 |
| Au | 1.60 |
| Pb | 29.00 |
| Bi | 11.00 |
| Sb | 3.27 |
| As | 3.18 |
| Te | 6.75 |
| S | 2.80 |

The difference of behavior of the various elements is surprising.

That a sample, which is not a correct average from a bar, or pig, of such copper, might lead to great errors regarding its silver and gold contents, needs no further illustration. But also the copper determinations would be far from being correct should they be made of a sample from any one part of such bar

or pig. This will at once become evident if we take the copper by difference (100 — amount of impurities) in the three analyzed samples:

| | Bottom. Per cent. | Center. Per cent. | Top. Per cent. |
|---|---|---|---|
| Copper by difference ..... | 99.618 | 98.841 | 99.263 |

Fig. 3 represents a block of refined converter-copper, with

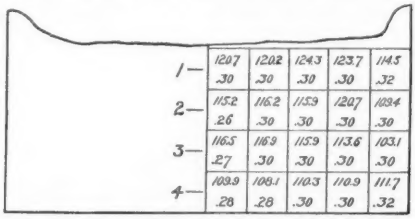


Fig. 3.—Block of Refined Converter-Copper with Determinations.

silver and gold as found in the respective samples.

General analyses were made of Sample 1, Samples 2 and 3 combined, and Sample 4, with the following results:

| | 1. oz. | 2 and 3. | 4. oz. |
|---|---|---|---|
| Ag ..... | 120.7 | | 109.9 |
| Au ..... | 0.30 | | 0.28 |
| | Per cent. | Per cent. | Per cent. |
| Bi ..... | 0.0026 | 0.0017 | 0.0013 |
| Sb ..... | 0.057 | 0.060 | 0.051 |
| As ..... | 0.022 | 0.021 | 0.014 |
| Te ..... | 0.008 | .... | 0.0056 |
| O ..... | 0.293 | .... | 0.200 |
| ($Cu_2O$ ..... ..... | 2.687 | .... | 1.800) |

Among copper metallurgists it is customary to give the amount of cuprous oxide instead of the oxygen. Both figures are, therefore, here inserted.

It will be noticed that the concentration of the precious metals and impurities in this second sample is analogous to the first; they have moved from the sides and bottom towards the center and top; but the degree of concentration is very much reduced. This may easily be explained by the fact that the refined copper contains a much smaller amount of impurities than the blister copper, thereby giving it a higher melting-point and a higher conductivity for heat, both properties favoring a more rapid solidification, and consequently shortening the time for the molecules to move towards the center.

Fig. 4 represents an original converter pig, from which

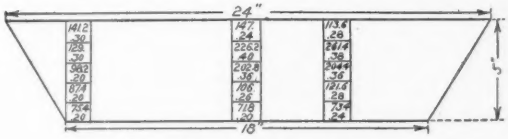


Fig. 4.—Converter Pig Copper.

kind of copper the previous sample was derived. The pig was drilled vertically, through the center. The values found for silver and gold show no variation, as to distribution, from the two other samples already illustrated.

Fig. 5 represents a refined copper, in which the amounts of

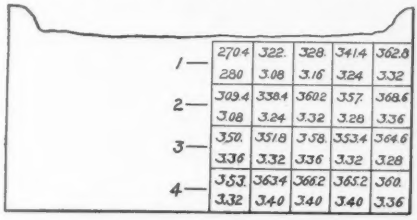


Fig. 5.—Refined Copper.

silver and gold, as well as the impurities, are considerably higher than in those represented by Figs. 2 and 3.

Samples 1, 2, 3, and 4 were analyzed as follows:

| | 1. | 2. | 3. | 4. |
|---|---|---|---|---|
| | Ounces. | Ounces. | Ounces. | Ounces. |
| Ag | 270.4 | 309.4 | 350.0 | 353.0 |
| Au | 2.80 | 3.08 | 3.36 | 3.32 |
| | Per cent. | Per cent. | Per cent. | Per cent. |
| Pb | 0.204 | 0.248 | 0.351 | 0.392 |
| Sb | 0.163 | 0.185 | 0.211 | 0.217 |
| As | 0.134 | 0.151 | 0.197 | 0.212 |
| Te | 0.0125 | . .. | 0.015 | 0.0195 |

Here, again, we see differences in the quantities of the elements in each sample; that is, concentration. But if we compare these with the former samples we observe the astonishing fact, that now we have the maxima in the position, where before were the maxima, and vice versa. In other words, we find a copper in which the conditions have been reversed. Instead of the precious metals and impurities concentrating towards the

center, it is now the copper which takes that place, and leaves the former concentrated towards the outside.

Fig. 6 represents a black copper from a blast furnace, but

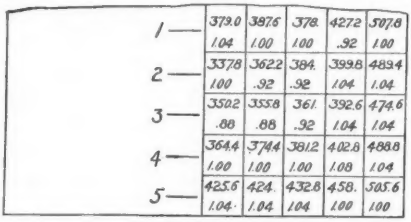


Fig. 6.—Black Copper Showing all Characteristics of Blister Copper.

showing all the characteristics of a blister copper. It is, in its relations to our subject, an analogon to the preceding sample.

Five samples were subjected to general analysis:

| | 1. Ounces. | 2. Ounces. | 3. Ounces. | 4. Ounces. | 5. Ounces. |
|---|---|---|---|---|---|
| Ag .... | 379.0 | 337.8 | 350.2 | 364.4 | 425.6 |
| Au .... | 1.04 | 1.00 | 0.88 | 1.00 | 1.04 |
| | Per cent. | Per cent. | Per cent. | Per cent. | Per cent. |
| Pb..... | 2.487 | 2.445 | 2.366 | 2.531 | 2.851 |
| Bi ..... | 0.400 | 0.360 | 0.360 | 0.310 | 0.420 |
| Sb..... | 3.438 | 3.073 | 2.820 | 2.789 | 3.929 |
| As..... | 0.705 | 0.716 | 0.630 | 0.627 | 0.706 |
| Te..... | 0.892 | 0.768 | 0.814 | 0.856 | 0.882 |
| S..... | 0.538 | 0.467 | 0.462 | 0.487 | 0.469 |
| Fe..... | 4.220 | 5.050 | 4.430 | 5.460 | 3.500 |

Scrutinizing the values for the various elements, it will be seen that sulphur and iron have behaved differently from the rest. Sulphur shows irregularities, while iron has concentrated towards the center; it has gone with the copper.

It will further be observed that the minimum amount of each element is not found in the same sample for all. In sample No. 2 we have the minimum for silver and tellurium; in No. 3 for gold and lead; and in No. 4 for bismuth, antimony, and arsenic.

The blocks of copper represented by Figs. 2 and 3 were comparatively low in their contents of precious metals and impurities, while those in Figs. 5 and 6 were comparatively high. The sample represented in Fig. 7 is low in precious metals, and high in impurities; yet we find that the silver has concentrated in accordance with the latter class. A general

| Slag and Matte | | | | | |
|---|---|---|---|---|---|
| | 59.6 | 59.2 | 60.3 | 60.4 | 61.3 |
| | 60.7 | 60.3 | 60.8 | 60.9 | 61.8 |
| | 60.5 | 60.8 | 61.2 | 61.3 | 61.6 |
| | 61.7 | 61.3 | 61.9 | 61.7 | 61.2 |

Fig. 7.—Black Copper.

furnace sample of this copper showed the following composition:

| | Ounces. |
|---|---|
| Ag | 62.2 |
| Au | 0.14 |
| | Per cent. |
| Pb | 0.78 |
| Bi | 0.0035 |
| Sb | 0.238 |
| As | 0.052 |
| Te | 0.0095 |
| S | 0.796 |
| Fe | 0.17 |

Fig. 8 is a photographic reproduction[1] of the face of *B* (Fig. 1) of the block of black copper represented in Fig. 6. It shows with the distinctness of a drawing each successive zone of solidification, by curved lines, or cavities, as well as the direction of solidification and concentration by straight linear cavities, which are perpendicular to the tangents of the curves, and which converge toward the center of solidification, the latter also being clearly indicated, much above the geometrical center, for reasons already given. The curved linear cavities were not readily discernible on the fresh cut, but were brought out plainly by rubbing with damp charcoal powder.

Reviewing the results obtained, they clearly prove the existence of two classes of copper-alloys. As already pointed out, in one class the foreign elements concentrate towards the center of solidification; in the other the copper concentrates to the center, while the foreign elements appear to have concentrated towards the outside.

Not a single element tested for has remained homogeneously

[1] For the photograph the writer is indebted to Mr. William Keyser, Jr., of Baltimore.

throughout, but the degree of uneven distribution varies with each one.

From data given in Hofman's Metallurgy of Lead, pp. 244 and 245, I conclude that this metal shows the same characteristics, in this respect, as copper. Also from an article by A. Raht in the Mineral Industry, 1894, p. 414. This writer gives a few instances in which he shows that silver and gold in base bullion bars are highest at the bottom and sides and lowest towards the top. He quotes Rosenlecher (from the Berg- und Hüttenmännische Ztg., Oct. 5, 1894) as having found exactly the reverse, and accuses the latter of strained figures, pet theories, etc. There seems no substantial reason for this inference, and undoubtedly Rosenlecher is as correct as Raht, and Raht as correct as Rosenlecher. The experiments of either covered but a narrow field, and neither discovered the other's side.

Very likely many of the alloys behave similarly, and homogeneity cannot be found with any of them.

Edward Mathey, in a publication in Nature, No. 1394, Vol. 54, calls attention to the fact that bars of gold, alloyed with zinc and lead, show very uneven distribution, gold having concentrated to the center and bottom, gravity being one cause.

To overcome difficulties in sampling such material, Mr. Mathey looks for a solvent and finds silver to be the medium. His figures cannot be pronounced as entirely conclusive, and the method proposed to obtain reliable samples is very circuitous, to say the least, although the trouble to be overcome is thereby minimized.

To come to the practical question of sampling, we must, from the stated and indubitable facts, draw the conclusion that it is almost impossible to obtain, from bars and pigs with irregular dimensions, by drilling, punching, or chipping, samples of satisfactory accuracy. As we have seen, concentration takes place from or towards every surface, and that in such bodies of metal a core, as it might appropriately be called, is formed, which is enriched or impoverished, as the case may be, and which in its shape does not conform to the outer surface. It is for this reason so difficult to obtain aliquot parts of the different portions of a bar or pig.

The root, then, of the difficulties of sampling, so often com-

plained of, lies in the irrational shape into which various metals are cast.

Another conclusion, which we must draw from observed facts, is the following: When we take from a molten mass of copper a sample by means of a ladle, the latter must be so hot as not to allow the forming of any solidified metal (sculling); for should this happen, the remaining liquid portion, which is to constitute the sample, would for one class of copper be too high in its contents of precious metals; for the other class it would be too low. If we pour from a ladle, in which the whole metal is liquid, a so-called shot sample, there is no reason assignable that it is not a correct sample. When large samples of shot are taken from charges, which are supposed not to be homogeneous, they must, of course, be remelted, and a smaller sample taken in the same way; or a sample plate must be cast, for which the rule below described must be observed, otherwise the final sample may become erroneous.

In most smelting and refining works sample-bars or cakes are desired, and to have these in the proper shape should be the duty of the sampler.

To eliminate all the difficulties inherent to pigs and bars, as above described, we only need reduce one dimension; or to state it more plainly, we cast a plate, whose thickness is small, compared to the other two dimensions. Of course concentration in this plate is governed by the same law as in any other body; it takes place from or towards the center, but the concentration in the horizontal direction, from the sides, can extend no farther than the distance equal to the thickness of the plate, for, when the solidification has proceeded that distance horizontally, the plate has entirely solidified vertically. We then have all around this plate a zone not wider than its thickness, where concentration has taken place just as in a bar or block; that is, horizontally and vertically, and consequently, we have one enriched and one impoverished band around the four sides. In the part of the plate enclosed by this zone we have had concentration in the vertical direction only, and the plate here, therefore, consists of what we may term layers of metal of different concentration. If we drill or punch through all of these layers we obtain a correct sample of the whole plate. This then seems the simplest solu-

tion of the sampling of any metal or bullion, and it is difficult to see any reasonable objection to the casting into plates of appropriate size of such material destined for shipment, of which subsequent sampling is required, and for which the remelting and taking of samples from furnace charges is impracticable. Uncertainty in sampling would be eliminated, and giving the plates beveled edges the handling thereof would not be more difficult than with bars.

Fig. 9 represents a plate of refined converter copper, fifteen

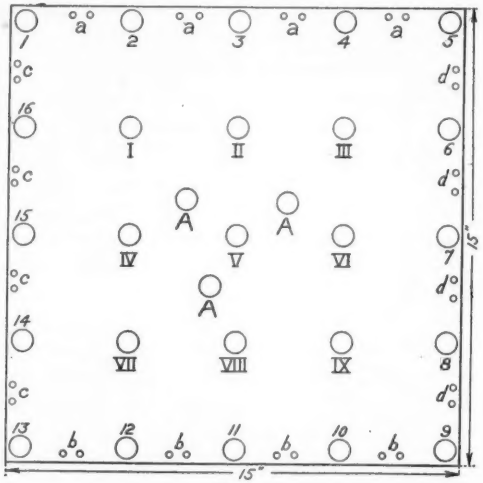


Fig. 9.

inches square by one inch in thickness. The holes designated by small letters were drilled with a one-quarter inch drill, one-fourth to one-eighth inch from the edge of the plate. The drillings from each side were collected in one sample, making the four samples, *a*, *b*, *c*, and *d*. The other holes were drilled with a three-quarter inch drill. Those designated by Arabic figures are from one-eighth to one-fourth inch from the edge. Those with Roman figures and the preceding ones were drilled through the plate. The three marked A were drilled about one-half inch deep, and the drillings collected for the top sample, then drilled through the plate, and the drillings taken for the bottom sample. The assays, in ounces per ton, were as follows:

$a = 105$, $b = 100.7$, $c = 101.7$, $d = 100.1$. Average $= 101.9$.

(1) $= 99.2$, (2) $= 103.2$, (3) $= 104.2$, (4) $= 99.8$, (5) $= 98.6$, (6) $= 97.8$, (7) $= 98.5$, (8) $= 99.3$, (9) $= 98.7$, (10) $= 98.9$, (11) $= 99.4$, (12) $= 99.4$, (13) $= 98.9$, (14) $= 103.7$, (15) $= 98.5$, (16) $= 99.5$. Average $= 99.85$.

I $= 98.4$, II $= 98.8$, III $= 98.9$, IV $= 97.6$, V $= 99.6$, VI $= 99$, VII $= 98.2$, VIII $= 99.4$, IX $= 99.5$. Average $= 98.7$.

A—top $= 99.9$, A—bottom $= 98$. Average, 98.9.

In the discussion of the theory of a thin plate it was pointed out that there must exist around the edge a zone of higher and one of lower concentration than in any other part of the plate, due to the horizontal and vertical movement of the molecules in this zone. The assays have demonstrated the correctness of that statement, although the zone does not appear to be strictly defined. This undoubtedly is due to temperature conditions of the mold and currents in pouring the metal.

The vertical concentration in the plate, inside the edge zone, is also clearly demonstrated by the top and bottom samples. These assays were repeated several times, while the rest were all made singly.

The samples and assays of the edge zone are, of course, incorrect representatives of the true contents of the plate and the furnace charge which it represents. The correct figure should be the average of I, II, III, IV, V, VI, VII, VIII, and IX $=$ 98.7, as also the average of A-top and A-bottom $= 98.9$, the two figures being indeed very close together.

The plate, from which the above figures are derived, was cast

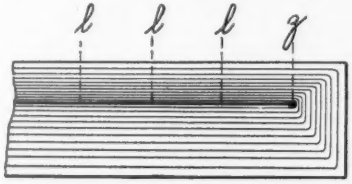


Fig. 10.—Vertical Section through the Edge and Part of Plate.

in a mold with very heavy bottom and thin sides. The solidification, therefore, took place much more rapidly from the bottom than from the sides and top. In Fig. 10 is illustrated this

process, it representing a vertical section through the edge and part of the plate. At *z* would be the highest or lowest point of concentration, according to the class of copper, the molecules meeting there from top, side, and bottom. At *l* would be the highest or lowest concentration of the layers, the molecules meeting from top and bottom.

For practical sampling, plates from eight to ten inches square are of ample size, but should not be more than one inch thick, and the drillings to be taken at least one inch from the edge through the entire plate.

After having seen how a correct shot sample or a reliable sample plate is obtained, let us now see how copper in its molten state is constituted.

The table below gives the results of tests, made for about three weeks, with furnace charges of from 90,000 to 110,000

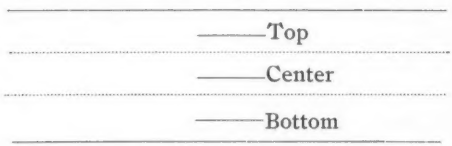


Fig. 11.—Position of Samples in Charge.

pounds of refined converter copper. The copper having been poled was, therefore, well mixed.

Sample plates were taken from the middle of every third of the charge, a practice adopted at these works. Fig. 11 illustrates the position of the samples in the charge.

| | Ounces of silver. | Average. | Ounces of silver. | Average. | Ounces of silver. | Average. | Ounces of silver. | Average. |
|---|---|---|---|---|---|---|---|---|
| Top..... | 106.7 | | 115.4 | | 113.0 | | 110.5 | |
| Center .. | 106.5 | 105.8 | 113.9 | 115.0 | 111.8 | 111.6 | 109.7 | 110.0 |
| Bottom.. | 104.3 | | 115.7 | | 110.1 | | 109.8 | |
| Top..... | 110.3 | | 109.1 | | 109.3 | | 108.2 | |
| Center .. | 110.2 | 109.9 | 108.9 | 108.7 | 108.4 | 108.8 | 108.1 | 108.1 |
| Bottom.. | 109.1 | | 108.1 | | 108.7 | | 108.1 | |
| Top..... | 107.8 | | 107.9 | | 107.4 | | 107.8 | |
| Center .. | 107.9 | 107.9 | 108.6 | 107.7 | 107.9 | 107.7 | 108.2 | 108.0 |
| Bottom.. | 107.9 | | 106.6 | | 106.8 | | 108.0 | |
| Top..... | 108.1 | | 108.5 | | 106.8 | | 105.8 | |
| Center .. | 108.1 | 108.1 | 108.8 | 108.5 | 106.9 | 107.0 | 106.8 | 106.4 |
| Bottom.. | 108.2 | | 108.1 | | 107.4 | | 106.5 | |
| Top..... | 106.9 | | 105.6 | | 101.2 | | 103.4 | |
| Center .. | 106.0 | 106.2 | 106.2 | 105.9 | 101.4 | 101.3 | 101.8 | 102.2 |
| Bottom.. | 105.7 | | 105.8 | | 101.4 | | 101.4 | |

The greatest irregularities occurred during the first few days, and were due to the furnace being new and the bottom seasoned with non-silver-bearing copper.

Each assay was made singly only and some of the differences may be attributed, therefore, to possible experimental errors, although nearly all are within the usual allowable limits in this kind of work.

The following are the values for silver and gold of three successive charges from a furnace of 30,000 pounds.

| | Ounces of silver. | Average. | Ounces of gold. | Average. |
|---|---|---|---|---|
| Top | 163.6 | 163.1 | 0.24 | 0.24 |
| Center | 163.2 | | 0.24 | |
| Bottom | 162.6 | | 0.24 | |
| Top | 363.9 | 363.2 | 2.92 | 2.95 |
| Center | 363.3 | | 2.96 | |
| Bottom | 362.5 | | 2.96 | |
| Top | 319.9 | 320.0 | 2.32 | 2.35 |
| Center | 320.1 | | 2.36 | |
| Bottom | 320.1 | | 2.36 | |

On the strength of these results, it is safe to say, that any charge of molten copper, once thoroughly agitated and mixed, is, and remains, uniform, and a sample taken from any part correctly represents the whole charge.

The subject treated is not only of practical importance, but has also a very interesting scientific side.

It is of course nothing new to find uneven distribution of the elements in an alloy, but that this distribution should follow within very narrow limits the quantities of these elements present in two diametrically opposite ways, as shown by the preceding experiments, is a subject which has not been discussed, and which is decidedly perplexing to explain. No law known to the writer would apply to this remarkable phenomenon.

As shown by the analytical figures, the impurities, in the cases where they have concentrated at the center, have a far higher degree of concentration than in the cases where they have gone towards the outside. This is readily explained. In the first case, the molecules move in the same direction as solidification takes place. They are, therefore, able to move and concentrate until the last particle of the metal is solid.

By the increase of impurities towards the center, the melting-

point of the alloy in that region is undoubtedly lowered, and thereby the solidification retarded, thus giving the elements more time to pursue their course.

In the case of concentration towards the outside, the elements move in the opposite direction in which solidification takes place, and by encountering the already solidified metal, their course is ended. The center being drained of impurities, its melting-point undoubtedly rises, accelerating the process of solidification, and reducing the time of motion and concentration.

That each element shows a different degree of concentration has already been pointed out. In explanation of this fact it might simply be said that it is due to the differences of affinity, which, of course, is true. But for the term "affinity" between metals we have as yet no expression in values or figures. We shall, therefore, attempt to find whether there is any relation between this and other physical properties of the atom of the respective elements, and shall, for that purpose, first consider the case of the copper as represented by Fig. 2, the differences here being best defined.

In the following table the elements are arranged in the order of their degree of concentration. $T$ = melting-point in °C; $A$ = atomic weight; $D$ = density, or specific gravity; $V = \frac{A}{D}$ = atomic volume.

| Element. | Concentration. | $T$. | $A$. | $D$. | $V$. |
|---|---|---|---|---|---|
| Pb | 29.00 | 332 | 206.4 | 11.38 | 18.1 |
| Bi | 11.00 | 265 | 210.0 | 9.82 | 21.4 |
| Fe | 6.75 | 500 | 126.0 | 6.25 | 20.2 |
| Sb | 3.27 | 437 | 122.0 | 6.70 | 18.2 |
| As | 3.18 | 500 | 74.9 | 4.70[1] | 15.9 |
| S | 2.80 | 115 | 31.98 | 2.04 | 15.7 |
| Ag | 2.59 | 969 | 107.66 | 10.50 | 10.2 |
| Au | 1.60 | 1037 | 197.0 | 19.30 | 10.2 |
| Cu | 0.992 | 1057 | 63.3 | 8.80 | 7.2 |

Comparing the degree of concentration with the melting-point we find a correspondence in a general way, the elements of low melting-point showing a higher degree of concentration than those of high melting-point. The sulphur forms a very marked exception to this rule.

[1] This is the density given for amorphous arsenic; for the crystalline form it is 5.67; consequently $V = 13.2$.

Between degree of concentration and either atomic weight or specific gravity there seems to exist absolutely no direct relation. Gravity in this case, therefore, can be no factor governing the distribution of the elements.

Finally, in the last column, the values for the atomic volume unmistakably show a similar arrangement to those for concentration. From this fact a law can be formulated (in the way of suggestion) reading as follows: "When, on the solidification of a metal (copper) the small amounts of impurities segregate, or liquate, and consequently concentrate towards the center, the degree of concentration is greatest for those whose atomic volume, compared with the atomic volume of that metal, show the greatest difference." Influence of other properties (melting point, etc.) would modify the law accordingly.

If the law expressed be true, we should then have for that class of alloys an alloy series of the metals, in which the latter are arranged according to their atomic volume:

| Element. | *V.* | Element. | *V.* | Element. | *V.* | Element. | *V.* |
|---|---|---|---|---|---|---|---|
| Ni..... | 6.7 | Rh..... | 8.6 | Au..... | 10.2 | Sn..... | 16.1 |
| Co..... | 6.9 | Ir ..... | 8.6 | Al ..... | 10.7 | Tl..... | 17.1 |
| Fe..... | 7.2 | Os..... | 8.8 | Cd ..... | 12.9 | Pb..... | 18.1 |
| Cu..... | 7.2 | Pt..... | 9.1 | Mg .... | 13.8 | Sb..... | 18.2 |
| Pd..... | 8.2 | Zn..... | 9.1 | In ..... | 15.3 | Bi ..... | 21.4 |
| Ru .... | 8.4 | Ag..... | 10.2 | | | | |

The theory thus deduced from an alloy of copper is, in the main, corroborated by an analysis of lead bullion by Schertel.[1] Elements (Cu, Fe, Zn), whose atomic volume differ most from that of lead, have concentrated in a higher degree than those which stand closer to the latter. Antimony, which is almost identical with lead in this property, has concentrated with that metal. Silver and bismuth do not appear to fall exactly in line.

In the class of copper, in which the impurities are found concentrated towards the outside, the above rule does not seem to apply, but owing to the small differences in the degree of concentration and consequent large influence of possible experimental errors, it would be too venturesome to attempt the establishment of another rule or law.

One fact observed in the copper represented by Fig. 6 seems also confirmatory of the theory expressed; namely, the concen-

[1] Hofman's Metallurgy of Lead, p. 244.

tration of the iron with the copper, both metals having the same atomic volume.

The following table gives the elements and their degree of concentration, as found in the above-mentioned copper, compared with the other physical properties.

The degree of concentration was obtained by dividing the values of the fifth sample by those of the third.

| Element. | Concentration. | *T.* | *A.* | *D.* | *V.* |
|---|---|---|---|---|---|
| Sb | 1.39 | 437 | 122.0 | 6.70 | 18.2 |
| Pb | 1.21 | 332 | 206.4 | 11.38 | 18.1 |
| Ag | 1.21 | 967 | 107.66 | 10.50 | 10.2 |
| Au | 1.18 | 1037 | 197.0 | 19.30 | 10.2 |
| Bi | 1.17 | 265 | 210.0 | 9.82 | 21.4 |
| As | 1.12 | 500 | 74.9 | 4.71 | 15.9 |
| Te | 1.08 | 500 | 126.0 | 6.25 | 20.2 |
| S | 1.02 | 115 | 31.98 | 2.04 | 15.7 |
| Cu | 0.987 | 1057 | 63.3 | 8.80 | 7.2 |
| Fe | 0.79 | 2080 | 55.9 | 7.80 | 7.2 |

The material on the subject discussed is, as yet, too scant to allow the drawing of positive conclusions. It should always be remembered by investigators that to give their work full scientific value, not only one or two elements in a combination of many, should be studied, but the interrelations of all must be observed.

BALTIMORE COPPER WORKS, DEC. 1896.

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[CONTRIBUTIONS FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE. No. 24.]

## RECOVERY OF WASTE PLATINUM CHLORIDE.

CONTRIBUTED BY H. W. WILEY.

Received January 26, 1897.

ALUMINUM turnings, freed of oil, have been used in this laboratory for some time for many purposes. Immediately after the publication of the paper of Wislicenus and Kaufmann[1] on the various applications of aluminum amalgam in the laboratory, a large quantity of these turnings was procured from the Pittsburg Reduction Co. Considerable difficulty was encountered in attempting to use these turnings in the manner described in the paper cited above. Mr. McElroy prepared the amalgam by washing aluminum clippings with ether to remove oil, treating with dilute caustic soda till free evolution of gas took place,

[1] *Ber. d. chem. Ges.*, **28**, 1323.

and then washing with water to remove the alkali. The solution of corrosive sublimate was made in alcohol (chosen because the most convenient solvent), diluted with water, and poured over the aluminum. When the evolution of gas was seen to take place from every piece of aluminum in sight, the mercuric chloride solution was decanted and the aluminum washed chloride-free with water. The treatment with soda and mercuric chloride was then repeated. Finally the turnings were washed free of water with strong alcohol. The washed amalgam in fresh portions of "absolute" alcohol kept up a steady evolution of gas, long after the time all water should have been removed. A portion was removed from the alcohol, washed with ether, and placed in petroleum ether, where the evolution of gas became quite strong. The containing flask was loosely stoppered and stood aside over night. In the morning the petroleum ether was gone.

A fresh portion of amalgam from 200 grams of aluminum was prepared and treated as before, except that the washing with alcohol was more thorough. The alcohol was removed with ether and the amalgam finally washed with kerosene. It was then covered with kerosene and stood aside. In about half an hour the evolution of gas became quite violent and the containing bottle hot. On cooling under the tap the generation of gas slackened, but on standing increased again as the mixture warmed up.

The kerosene was such as is used for lamps. It gave a black zone of lead sulphide when treated with the lead acetate test. It is very likely Lima oil. As is well known in the Frasch process of purifying, the oil is passed through copper oxide, which it converts into copper sulphide. As for every atom of sulphur removed an atom of oxygen must go into the oil, probably the action of the aluminum consisted in appropriating this oxygen. Neither bright sodium or sodium amalgam had any special action on the kerosene used. The action of the amalgam on strong alcohol has been confirmed by Hillyer.[1] We have been able to use these turnings, amalgamated with mercuric chloride, for the reduction of nitrates to ammonia for analytical and other purposes, and it is probable that a speedy and accurate analytical process may be elaborated on this line. We

[1] *Am. Chem. J.*, **18**, 621.

have, however, found the most successful use of the turnings in the recovery of platinum waste. This method of recovery is due to Mr. K. P. McElroy, and has been worked out by him in detail, and has been successfully used for some time in the recovery of platinum chloride waste from potash analyses. The method is as follows:

The waste platinum from potash determinations is collected and to the hot water solution of platinum potassium chloride is added aluminum in the form of clippings or turnings. In a few minutes a platinum-aluminum couple is formed and reduction goes on vigorously. The addition of hydrochloric acid is not necessary, but is advisable for promoting the settling of the platinum formed. After the reduction is complete, more hydrochloric acid is added to dissolve the excess of aluminum. When this is done the platinum will be found to settle and the supernatant liquid will be clear. The supernatant liquid contains but little suspended platinum, but it is passed through a large folded filter. If it does not come through clear, as is sometimes the case, return it a few times. As but little platinum gets on the filter, the same filter is used over and over again for successive filtrations until enough platinum accumulates to make its recovery worth while. When the clear liquid is all decanted, add water to the spongy platinum, shake, allow to settle, and decant. Repeat this until the supernatant liquid is free of chloride. The spongy platinum is then covered with strong nitric acid and heated for the purpose of removing copper. Aluminum often contains a little copper, which of course remains with the platinum. When the copper is all dissolved the copper nitrate and the excess of nitric acid are removed by washing with water by decantation as before, till the supernatant liquid is acid free when tested with Congo paper. The resulting platinum black is dissolved with aqua regia, made by mixing five parts of hydrochloric acid with one part of nitric, added in amount sufficient to dissolve all of the platinum present. The solution thus obtained is transferred to a porcelain dish and evaporated on a steam bath till a portion taken out with a rod solidifies on cooling. The residue is diluted with water and hydrochloric acid and re-evaporated. If, on adding water to the sirupy mass formed by this evaporation, nitrous vapors are

evolved, add plenty of water and re-evaporate. Repeat this evaporation with water till the nitrous vapors are no longer evolved on dilution. Finally dilute sufficiently to filter and add water until the color of a platinum chloride solution of known content is matched.

## STANDARD IODINE SOLUTION FOR SULPHUR DETERMINATIONS.

By Edward K. Landis.

Received January 11, 1897.

THE following calculation shows an easy method of preparing Payne's iodine solution, with the least amount of calculation.

REACTIONS.

$K_2Mn_2O_8 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$.

$K_2Mn_2O_8 + 10KI = 10I + 6K_2O + 2MnO$.

$H_2S + 2I = 2HI + S$.

2 atoms I = 2 atoms Fe = 1 atom S.

32 grams S = 112 grams Fe.

1 gram S = 3.5 grams Fe.

When five grams are taken for analysis, 0.01 per cent. = 0.0005 gram, and this multiplied by 1000 = 0.5 gram in a liter.

Let $x$ = value of 1 cc. $K_2Mn_2O_8$ in Fe in grams.

Then $\frac{0.5}{\frac{x}{3.5}} = 0.5 \times \frac{3.5}{x} = \frac{1.75}{x}$.

Therefore 1.75 divided by the value of one cc. potassium permanganate in iron in grams, gives the number of cc. of potassium permanganate to be added to the potassium iodide and sulphuric acid and diluted to one liter, to form iodine solution of such strength that one cc. will be equal to 0.01 per cent. sulphur when using five grams of sample.

## NOTE.

*Notes on "An Analytical Investigation of the Hydrolysis of Starch by Acids."*[1]—A number of errors and misprints were overlooked by the authors in their compilation of this paper. The following are the most important:

[1] This Journal, 18, 869.

Page 873, ninth line, read "77.40" instead of "76.40."

Page 873, second foot-note, read "Heron" instead of "Hearn."

Page 879, the equation for the curve of $K_{386}$ is much more nearly: $x^2+y^2-758\,x+772.4\,y=0$. The values of $K$ as given in Table C are, however, correct.

Page 880, last equation should read $m=\dfrac{\alpha+141.5\,K-195}{26.52}$

By a clerical error the denominator 27.82 was carried through the calculations of Tables C and E. The values of $m_{386}$ are, therefore, too low by 4.65 per cent. of the true value, the maximum therefore being 0.462 instead of 0.441. The values of $g_{386}$ and $d_{386}$ are correspondingly too high. This error does not affect the general conclusions of the article nor the character of the curves plotted in Plate B. The final resulting values of Tables I, II, and III, deduced from Table E, are moreover not materially changed by the correction.

Page 885, twenty-third line, the "$\alpha_{D_{386}}$" should be "131.7," the $K$ (obtained) should be "0.523," the $K_{386}$ (calculated) should be "0.533."

Page 885, third line from bottom read "possibly" instead of "possible."

Page 896, eleventh line, read "$\frac{1}{50}\,N$" instead of "$\frac{1}{100}\,N$."

Page 890, Table II, Column II, read "134.0" and "285.0" instead of "13.40" and "28.50."

Page 897, Plate I, the last plot should be five divisions to the right.

It is interesting to note that if there were but two simple carbohydrates resulting from hydrolysis, dextrose, and dextrin, as believed by some investigators,[1] the theoretical values of $K$ would fall exactly on a *straight line* passing through the "zero" and "hundred" points of Plate A. The *experimental* values, on the contrary, show a maximum divergence from this line of about eight per cent., a discrepancy too great to be explained by experimental error or approximate specific gravity standard. Moreover, at the higher conversions, the curve approaches the value of pure dextrose again, showing quite conclusively that a body which we take as maltose, is an intermediate product between dextrin and dextrose, and not a decomposition product of dextrose, at least as far as the curve is carried.

[1] Flourens: *Compt. Rend.*, 110, 1204–1206.

Plots on a similar scheme made of the values of dextrin and maltose, present at successive stages of diastase conversion $[\alpha]_{D386} = 195$ and $[\alpha]_{D386} = 135.2$, demonstrate that by the law of Brown and Morris, $K$, $m$, and $d$ can be graphically represented as straight lines.

Again it follows that the values of $K_{386}$ of a *mixture* of hydrolyzed starch products made by the action of acids must be necessarily less than the value of $K$ of a homogeneous product of the same rotation, as it falls on the straight line joining the points on the $K$ curve corresponding to the original values of the separate constituents.

A reprint of the paper on the hydrolysis of starch will appear in the *Technology Quarterly* in March. The authors will be glad to send corrected copies to any member of the Society interested in the subject.

GEO. W. ROLFE.
GEO. DEFREN.

## NEW BOOKS.

COMMERCIAL ORGANIC ANALYSIS. BY ALFRED H. ALLEN, F.I.C., F.C.S. Second Edition, Revised and Enlarged. Vol. III. Part III. VEGETABLE ALKALOIDS (Concluded), NON-BASIC VEGETABLE BITTER PRINCIPLES, ANIMAL BASES, ANIMAL ACIDS, CYANOGEN AND ITS DERIVATIVES. xii + 508 pages. 1896. Philadelphia: P. Blakiston, Son & Co. Price, $4.50.

This, the last volume but one of Allen's compendious work, is devoted to a study of the vegetable alkaloids, non-basic vegetable bitter principles, animal bases, animal acids, and cyanogen and its derivatives. It is really Volume V of the book, Volume III having grown into three large volumes during compilation and publication.

This volume, like its associates, is much more than its title indicates. It not only describes methods of procedure for the benefit of the analyst, but gives also a description of the various organic bodies, notes concerning their preparation and other encyclopedic matter valuable to the scientific reader.

Since Mr. Allen's work has so far outgrown its original plan, it might be well for him to consider the advisability of a re-arrangement of the material in a future edition in order to make it more convenient for different classes of chemical workers. For instance, in the present volume the matter on pages 1 to 166 is

of especial interest to pharmacists and toxicologists, pages 192 to 423 to physiological chemists, and pages 424 to 486 to manufacturing and technical chemists. The section embraced in pages 167 to 191 is of especial interest to chemists connected with the brewing industry. It is easy to realize, however, that the best arrangement of all the helpful matter which Mr. Allen has brought together is quite as much of a problem as the treatment of the subject-matter itself. Of the latter the previous volumes are witnesses of the great success which has attended the laborious and long-continued efforts of the author in culling from the scattered chemical literature of the whole world the facts and processes most useful to the busy worker in the various fields of chemical industry embracing the study of organic bodies. If it were possible to distinguish those organic bodies which are important from those of an opposite character, it might be said that Mr. Allen has included many things in his book which are not valuable from a commercial point of view. For instance, there is very little demand for adoninin, bilirubin, cevine, urinary deposits, euonymin, gall-stones, furze, hippuric acid, indican, jervine, kynurine, melan, nataloins, ophelic acid, piuri, rottlerin, quadri-urates, serpents' urine, taurocarbamic acid, urea, verine, and xanthocreatinin. These and hundreds of others are of so little commercial importance as to render questionable the utility of extending the volume to comprehend them. The description of these bodies would find a more fitting place in encyclopedias, kept for occasional reference, than in a practical manual to be consulted daily by the busy worker.

To the pharmacists the articles on the vegetable alkaloids will be found of useful interest. The physiological and agricultural chemists will welcome the articles on the potato, hops, and animal bases, the medical chemists the one on animal acids, and the manufacturing chemists the chapter on cyanogen.

It is doubtful whether asparagin, glutamin, betain, cholin and lecithin should be classed with the animal bases. These bodies are, first of all, products of vegetable metabolism, and their occurrence in the animal economy is quite as likely to be due to their ingestion in the food as to the results of any vital activity of the organs of the animal body.

The chapter on Hop Substitutes will prove of interest to American chemists and brewers at the present time, when so many of the State Legislatures, and even the National Congress are considering the subject of legislation looking to the definition of beer, and a description of its adulterants. We have in this country, as in England, no legal definition of beer, and in the absence of such a definition, the brewer using quassia wood instead of hops, could not legally be accused of practicing adulteration. In point of fact it is doubtless true that hop substitutes are used to a very limited extent in this country. Nevertheless, our chemists will be grateful to Mr. Allen for presenting in a succinct form the best methods of detecting the various bitter principles which have been proposed and used for hop substitutes. I am glad to see that he gives no credence to the absurd statement we all have heard, relating to the presence of strychnin in beer.

The article on urea is very full and complete, but inasmuch as the author has published a special treatise on urine analysis, and for the additional reason mentioned above, that urea has no great commercial importance, space would have been saved by its omission.

We shall welcome Mr. Allen's concluding volume, and the work when complete will find a place with that of Fresenius in the equipment of the analytical chemist. H. W. WILEY.

A BRIEF INTRODUCTION TO QUALITATIVE ANALYSIS. By LUDWIG MEDICUS, Professor of Chemistry in the University of Würzburg. Translated from the Fourth and Fifth German editions, with additions by John Marshall, Assistant Professor of Chemistry in the Department of Medicine of the University of Pennsylvania. Fourth Edition. 203 pp. 8vo. Philadelphia: The J. B. Lippincott Co. Price $1.50.

The writer of a book upon qualitative analysis at the present time finds it difficult to avoid following beaten paths. In fact, the methods given in the earlier text-books for the qualitative testing and separation of bodies have survived so many attempts to improve upon them, and the difficulties in the way of material innovations have usually proved to be so great, that it is hardly to be expected of an author that he should originate wholly new methods of qualitative work. Superior arrangement of topics, greater clearness and accuracy of details, and the presentation of known facts in such manner as to call for more vig-

orous exercise of the student's thinking powers constitute commonly the points of advantage claimed for any new book designed to replace older ones in elementary chemical analysis.

As regards accuracy, clearness, and mode of presentation, the English version of Medicus' book fulfils its purpose in a very satisfactory manner. The descriptions of processes are explicit and yet concise, and wherever possible are supplemented by tabulated statements. Useful data are given as to solubilities of precipitates. The rarer elements are separately treated in an appendix, and, for the further illustration of their reactions, analyses of their more important ores are described.

As regards arrangement, many teachers will find no objection to the book. The author's system of classification of bases is the same as that adopted in various other text-books, but this classification, according to which the metals precipitated by hydrochloric acid are treated first in order, as group one, and the alkali metals with magnesium are considered last, as constituting group six, has some disadvantages. The student on entering upon a laboratory course has much to learn regarding the nature of salts, and he gains a clearer idea of these if he experiments upon the compounds of the alkaline and alkaline earth metals before taking up the study of mercury, antimony, and tin. The greater simplicity in the reactions of the light metals is an additional reason why they should precede the heavy metals. The work of the translator has been well performed.

On account of its attractive form and its simple and clear directions and explanations, this book will prove a valuable aid to students of analytical chemistry. FRANCIS C. PHILLIPS.

LECTURE NOTES ON THEORETICAL CHEMISTRY. BY FERDINAND G. WIECHMANN, PH.D., Columbia College. Second edition. Revised and enlarged. xviii+288 pp. 1895. New York: John Wiley & Sons. Price, $3.00.

The favorable reception accorded the first edition has led the author to issue a second edition of the "Lecture Notes on Theoretical Chemistry." The matter has been carefully revised and such additions made as serve to keep the student in touch with the most recent developments of chemistry, especially in the field of physical chemistry. The space given to stereochemistry

has been doubled and additions have been made to the excellent bibliography, which include important publications since the appearance of the first edition. The book is neatly printed and is quite free from typographical errors.

It is a matter of regret that in a revised work the subject of valence has not been treated differently. The classification of elements as artiads or perissads is unnecessary and misleading. While it is true that variations in valence usually proceed by twos, yet there are such well-defined exceptions, based upon vapor density determinations of the molecular weights of compounds, that we cannot feel justified in making the assumption that "two bonds neutralize each other." Indeed, does such an assumption really explain anything? Certainly, it is a questionable good when it leads to such illustrations as those used in the text to represent a monad, a dyad, etc. CHARLES H. HERTY.

PRÉCIS D'ANALYSE CHIMIQUE—(I) ANALYSE QUALITATIVE, pp. 190. (II) ANALYSE QUANTITATIVE, pp. 312. By E. FINK. Small 12 mo. Paris: Carré et Naud, Editeurs. 1896.

It is indeed refreshing to find a French chemistry which does not write water HO (in view of which we can pardon the continuance of Fl, Az, Bo, and St), and in which the reactions are uniformly well written and correct according to the modern standards. The French "devil," however, is responsible for many typographical errors, one of which deserves mention even in this brief review: "anhydride chromique" is metamorphosed into "anhydride chro*n*ique."

Part I is well done, the liberal use of different styles of type bringing the classification out clearly, the whole being put in good form for beginners to take hold of. It is regrettable that the chapter on dry tests was not made more complete, since it is well stated as far as it goes; the classification and treatment of the acids is particularly good. Part II cannot be so freely praised. The writer has attempted the impossible, even the undesirable. To condense the whole field of quantitative analysis into small space, is *necessarily* to sacrifice accuracy for brevity, to leave out all the fine points, to omit comparisons of methods and discussions of their limitations, and what kind of a chemist is he who is not taught these *from the beginning?* Such quantitative analysis as is put forth here, without criti-

cism of methods described, without the well-known precautions fully stated, would engender a chemist whose work would be of no value to himself or to anyone else. Part I will advance the true science of chemistry in France; Part II will hinder it.

JOSEPH W. RICHARDS.

STUDIES IN CHEMICAL DYNAMICS. BY J. H. VAN 'T HOFF. Revised and enlarged by DR. ERNST COHEN. Translated by THOMAS EWAN, M.Sc., Ph.D. Large 8vo. vi + 286 pp. Easton, Pa.: Chemical Publishing Co.; Amsterdam: F. Muller & Co.; London: Williams & Norgate. 1896. Price, $2.50.

Few works in chemistry have been more stimulating in their nature, and more productive of extended investigation of the most important character, than the simple, unpretentious "Études de Dynamique Chimique," which van 't Hoff published in 1883. It is a matter of general congratulation that a new edition of this work has appeared, and furthermore that it has been promptly issued in an English translation.

The volume before us possesses all of the attractions characteristic of its predecessor. It is not a text-book. It is simply an admirable monograph dealing with several of the most fundamental problems engaging the attention of the rapidly increasing number of chemists specially interested in the determination of the laws governing the rate of chemical change, the measurement of chemical affinity, and the general topic of chemical equilibrium. While these three subjects are not treated exhaustively, they are still discussed so fully that no better handbook could be used for guidance in the fields of research in question. The fullness of description, the ample details on apparatus for experimental investigation, the wealth of illustrations, the charms of the mathematical deductions, all render the volume simply invaluable, certainly for the beginner, and possibly for the more advanced worker in physical chemistry.

Some of the leading features of this new edition are: the recent work on the tartrates; the discussion of Cohen's concentration cell; the calculation of the change of solubility with the temperature; the summary of all known methods for determining inversion temperatures; the elaborate and instructive researches on the oxidation of aldehyde, phosphorus, and sulphur; the many new data on the change of the equilibrium constant with

the temperatures; the effect of pressure on condensed systems; and the detailed discussion of the methods of determining the transition temperature.

It is to be regretted that several important phases of the general subjects have not been brought into discussion: the topic of catalytic actions; the applications of the electrolytic dissociation theory to the phenomena of equilibrium; the translator's own admirable work on the freezing-points of sulphuric acid solutions; the author's extended investigations on dilute solutions; and several others.

Here and there the need of more careful proof-reading is evident. The general typography of the book is, however, exceptionally fine, and the illustrations most effective. The fullness of the bibliographic features is particularly commendable. As we welcome so admirable an aid and guide to experimental work in physical chemistry, we cannot but regret that, thus far, there are so few centers in our own country, where the factors of experience, instrumental equipment, and enthusiasm combine to render America a noteworthy contributor in this field. Many indications, however, point to a rapid and early improvement in this respect. THOMAS H. NORTON.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. By HARVEY W. WILEY, Chemist U. S. Dept. of Agriculture. VOL. III, AGRICULTURAL PRODUCTS. xii + 665 pp. Easton, Pa.: Chemical Publishing Co. 1897. Price $3.75.

This volume completes the most exhaustive work ever published on agricultural analysis. One of the sub-titles states that it is a manual for the examination of soils, fertilizers, and agricultural products. It is more properly a treatise on these subjects.

The volume under review is arranged in seven parts. Part I deals with the collection, preparation, and preservation of samples, the drying of organic bodies, the determination of ash, and the general description of the objects and methods of extraction by solvents. The full discussion of the subject of collecting and drying samples is timely and if the suggestions of the author had been more generally followed, the analyses of agricultural products that are found in various works of reference would have had a far greater value.

Parts II and III deal with the carbohydrates; Part II with sugars and starch in comparatively pure forms, while Part III deals with all carbohydrates in crude or manufactured products. These two parts comprise 250 pages and contain an enormous amount of information. Here the principles, as well as the practice, are well brought out. Numerous and extended tables of valuable factors are put where they are needed and the twenty-seven formulas for "Fehling's solution" will be appreciated by those who have had occasion to search chemical literature with only an author's name for a guide.

These sections include the more recent analytical methods for separation of the substances that are usually determined by difference and reported under the negative term of nitrogen-free extract.

Part IV is devoted to the examination of fats and oils. The physical methods are well represented while the best of the somewhat empirical methods for preliminary examination and identification of various oils and fats are very satisfactorily described and a good estimate of their comparative value is given. A considerable portion of this part of the work is devoted to descriptions of methods which are to be used in the examination of products that are more fully treated of in the last two parts of the volume.

The separation and estimation of bodies containing nitrogen which constitute Part V will prove of great interest and value to all chemists who are called upon to deal with animal and vegetable products. The results of much recent work on proteids are included here and the whole matter is presented in a far more satisfactory and systematic manner than is to be found in any other work in English.

The full treatment of the subjects in the first five parts enables the author to condense into less than eighty pages of Part VI an enormous amount of information on the subject of the examination of dairy products. Here we find all the important short cut methods for partial milk analysis and a very excellent discussion on the investigation of other dairy products.

If there is anything in the line of agricultural analysis that one cannot find elsewhere, he will find it in Part VII, which is devoted to miscellaneous agricultural products. Into 100 pages

is put a mass of explanations and directions for the examination of practically all agricultural products that, taken in connection with the previous volumes and parts of this work, constitute a veritable working library of agricultural analysis. The work is illustrated with many cuts, plates, and sections of apparatus, those on optical apparatus being especially full and clear.

There has been a slight tendency to criticise the work as being too full and as not pointing out select methods. The author forestalls this thought in his preface and must be congratulated on standing by his original purpose of presenting to the busy worker a broad view of a great subject.

The volume closes with the bouquet of fermented and distilled liquors, and no one will begrudge the author these delights at the close of his arduous and valuable work.

H. A. HUSTON.

A MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS FOR THE USE OF STUDENTS. BY FREDERICK A. CAIRNS, A.M. Third edition, revised and enlarged, by ELWYN WALLER, Ph.D. New York: Henry Holt & Co. 417 pp. Price, $2.00.

The unusual success that "Cairns' Manual of Quantitative Analysis" has won is doubtless largely owing to the attention given in it to the details of manipulation. It is not enough to tell a student of quantitative analysis what to do; he must be told how to do it. To write a book on this subject that will stand the test of laboratory use by students, one must be both a skillful analyst and an experienced teacher.

In the new edition, which has been largely rewritten by Dr. Elwyn Waller, several changes have been made. The chapters on "Proximate Analysis" have been cut out, and the scope of the work restricted to "Mineral Analysis;" a wise step, as the analysis of organic substances has been so largely extended, and has become a special subject with a literature of its own. Dr. Waller's excellent and useful paper on the "Properties of Precipitates" has been added, and the list of tables in the appendix has been increased. Under "Manufactured Irons" are described the colorimetric method for combined carbon, Stead's alkali method, Drown's method for silicon, the rapid volumetric method for phosphorus, Carnot and Drown's, and McKenna's methods for aluminum, and Lundin's method for arsenic. Under "Min-

eral Water" Gooch's method for boric acid is given. Under "Fertilizers" the methods of the Association of Official Agricultural Chemists are quoted, and the Lewis-Thompson calorimeter is explained in determining the heating power of coal.

While to a professional analyst grammatical style may not seem of great importance, there can be no doubt about its importance to the student. He is frequently assured that accuracy of thought and lucidity of diction are characteristics of the truly scientific mind; but the vague, involved, and verbose style of more than a few of our chemical text-books cannot fail to make him doubt whether their authors possessed either accuracy or mental lucidity. In the present work, however, the clearness of the directions and the excellence of the grammatical style are worthy of commendation and imitation, while the printing and make-up of the book are creditable to the publisher. The new edition of the "Cairns-Waller Manual" will beyond a doubt be even more successful than the former one.

PETER TOWNSEND AUSTEN.

ENGINEERING CHEMISTRY: A Manual of Quantitative Chemical Analysis for the Use of Students, Chemists, and Engineers. BY THOMAS B. STILLMAN, M.SC., PH.D., Professor of Analytical Chemistry in the Stevens Institute of Technology. With illustrations. Easton, Pa.: Chemical Publishing Co. 1897. xxiii + 523 pp. Price $4.50.

This volume will be found of great utility to the analytical chemist, and especially to him whose chief work comprises the examination of the materials of engineering. It contains a mass of most valuable data conveniently and compactly arranged, much of which is original and much of which was heretofore, for the most part, only to be found scattered through the files of periodical literature, or else in text-books relating to some special branch of the subject, and which has therefore only been available to the general analyst or to the chemical engineer as the result of more or less elaborate research.

Not only are described in detail nearly all of the conventional methods of analysis applicable to the various materials of engineering, such, for example, as the metals, alloys, cements, paints, oils, fuels, gases, water, etc., but many physical and mechanical tests in general use are clearly set forth, as, for instance, the mechanical testing of Portland cement, physical tests

of building stones, physical examination of lubricants, photometry, pyrometry, etc., and not the least valuable portions of this work are the elaborate examples which the author gives, showing methods of calculation whereby the results of analysis are utilized in practical work as, for example, in the calculation of blast-furnace charges, or in determining the heating power of fuels and gases.

While, as is to be expected, there is nothing particularly new in most of the processes given, many of them are more or less modified in some of their details which is doubtless due to the wide and varied experience of the author. It is to be regretted, however, that the description of some very valuable analytical methods which certainly should be included in a work of this character, are omitted, notably, for instance, the titration of iron salts with potassium permanganate, determination of $Pb_3O_4$ in red lead, and the determination of the well known "saponification equivalent" in the analysis of oils.

The value of the work as a text-book for the instruction of students is to a certain extent impaired by reason of the fact that *theoretical principles* upon which the analytical processes are based are not sufficiently elaborated. This defect is, however, common to nearly all systems of instruction in analytical chemistry, especially in quantitative analysis, but does not to any extent impair the value of this book to the working chemist, although the system, upon which the subjects treated of are arranged, is susceptible of considerable improvement. The arrangement of the more complex methods in the form of "schemes," although not especially new is particularly worthy of commendation.

The volume is profusely illustrated and is furnished with a very complete table of contents and index, besides copious footnotes referring to original publications, as well as a large number of extremely useful tables, many of which appear to be original.

This book should find a place as a standard of reference in the working library of every analytical chemist and chemical engineer, and should, as it deserves, go through many future editions when such minor defects as it now contains will doubtless be corrected.

J. H. WAINWRIGHT.

## BOOKS RECEIVED.

Commercial Organic Analysis: A treatise on the properties, proximate analytical examination, and modes of assaying the various organic chemicals and products employed in the arts, manufactures, medicines, etc. By Alfred H. Allen, F.I.C., F.C.S. Second Edition, Revised and Enlarged. Volume III, Part III. Vegetable Alkaloids (concluded), Non-Basic Vegetable Bitter Principles, Animal Bases, Animal Acids, Cyanogen and its Derivatives. 1896. Philadelphia: P. Blakiston, Son & Co. xii + 508 pp. Price, $4.50.

Iron Making in Alabama. By William Battle Phillips, Ph.D. Alabama Geological Survey, Montgomery, Ala. 1896. Jas. P. Armstrong, Printer. 164 pp.

The Constants of Nature. Part V. A Recalculation of the Atomic Weights. By Frank Wigglesworth Clarke. New Edition, Revised and Enlarged. 1897. pp. vi + 370. City of Washington: Smithsonian Institution. Price, $2.00.

A Simple Method of Water Analysis. By John C. Thresh, M.D., D.Sc., D.P.H. 47 pp. Philadelphia: P. Blakiston, Son & Co., and London: J. & A. Churchill. 1897. Price, 88 cents.

Notes on Assaying. By P. de Peyster Ricketts and E. H. Miller. New York: John Wiley & Sons. viii + 311 pp. Price, $3.00.

The Carbohydrates of Wheat, Maize, Flour, and Bread, and the Action of Enzymic Ferments upon Starches of Different Origin. By Winthrop E. Stone, Ph.D. Bulletin No. 34, U. S. Department of Agriculture. Washington: Government Printing Office. 1896. 44 pp.

Laboratory Calculations and Specific-Gravity Determinations. By John S. Adriance, A.M. Third Edition, Revised and Enlarged. ix + 144 pp. New York: John Wiley & Sons. 1897. Price, $1.25.

Notes for Chemical Students. By Peter T. Austen, Ph.D., F.C.S. Second Edition. vi + 111 pp. New York: John Wiley & Sons. Price, $1.50.

Manures and Fertilizers. (1) Report on the Enforcement of the Fertilizer Control Law. (2) Fertilizer Tests with Wheat. (3) The Waste of Farm Manures. (4) Green Manuring. Bulletin No. 34. University of the State of Missouri, Columbia, Mo. April, 1896. 35 pp.

Prècis d'Analyse Chimique. By E. Fink. Première partie. Analyse Qualitative. 1896. 190 pp. Paris: Georges Carrè, éditeur.

Précis d'Analyse Chimique. By E. Fink. Deuxième partie. Analyse Quantitative. Avec 60 figures dans le texte. 312 pp. Paris: Georges Carré et C. Naud, éditeurs.

Traité Élémentaire de Chimie. By A. Haller and P. Th. Muller. Chimie organique. 205 pp. 1896. Paris: George Carré et C. Naud, éditeurs.

Traité Élémentaire de Chimie. By A. Haller and P. Th. Muller. Chimie Minérale. 336 pp. 1896. Paris: Georges Carré, éditeur.